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THE UNIVERSITY OF ALBERTA

RECLAIMING OF SOILS MADE BARREN BY SULFUR
FROM GAS PROCESSING PLANTS

by



Ronald A. Bertrand

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
MASTER OF SCIENCE

DEPARTMENT OF SOIL SCIENCE

EDMONTON, ALBERTA

FALL, 1973

THE UNIVERSITY OF ALBERTA
FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled "Reclaiming of soils made barren by sulfur from gas processing plants", submitted by Ronald A. Bertrand in partial fulfilment of the requirements for the degree of Master of Science.

ABSTRACT

A number of natural gas processing plants in Alberta have experienced a soil acidity problem, near the plant site, due to oxidation of elemental sulfur (which is a product of gas processing) blown from sulfur stockpiles and deposited on the soil. Preliminary experiments at Innisfail, conducted previous to this investigation, showed that liming restored plant growth to a soil which had been acidified to pH 3.7 by sulfur. The present study was conducted with soils from near a gas processing plant at Waterton, where soils had been very severely acidified (as low as pH 2.0). Experiments were undertaken to find if various acidified soils from Waterton could be reclaimed by liming; and to compare different types of liming materials, and methods and rates of application.

From these experiments it was found that liming with high rates of CaCO_3 applied to a number of severely affected soils promoted a normal amount of plant growth in both the field and greenhouse. After CaCO_3 was added to sulfur-acidified soils, plants were sown immediately and grew well. Thus these soils were immediately reclaimed by neutralization of soil acidity by CaCO_3 .

Greenhouse, incubation, and field experiments were undertaken to determine the form and amount of lime best

for reclaiming soils varying in acidity and containing different levels of unreacted elemental sulfur. $\text{Ca}(\text{OH})_2$ applied at rates that exceeded the soil lime requirement, raised the soil pH to a level (up to pH 12.0) that prevented plant growth. However, chemically equivalent amounts of CaCO_3 neutralized the soil acidity as quickly as did $\text{Ca}(\text{OH})_2$ and did not raise the pH above 7.5. Excess CaCO_3 did not harm plant growth and, also, compensated for potential acid production due to stimulation of sulfur oxidation as a result of liming. CaCO_3 alleviated the salinity problem due to high sulfate levels prevalent in sulfur-acidified soils while MgCO_3 did not lower the salinity of the soils. Heavy rates of CaCO_3 promoted good, normal plant growth on an array of acidified soils.

Lime applications to a soil depth of six inches, slowly began to diffuse downward neutralizing acid subsoil. Surface applied lime had little effect on sub-surface soil pH.

The results of studies in which elemental sulfur was added to normal, limed, and acid soils indicated that large amounts of sulfur (up to 9,000 ppm) were oxidized and soil pH lowered (down to 2.5) in a short period of time (12 weeks). The sulfur oxidation was most rapid in a limed soil that was previously acidified.

Chemical analysis of acidified, limed, and unaffected

soils demonstrated that liming eliminated the toxic levels of extractable Al and Mn present in acid soils, lowered the chemically extractable P, drastically increased the Ca:Mg ratio, somewhat reduced the very large amount of soluble SO_4 in sulfur-acidified soils, and restored the nitrifying ability of acidified soils. Also, N mineralization in acid soils was almost the same as in limed soils, when comparing mineral N accumulation after incubation.

Chemical analysis of oats and barley grown on acidified (pH 3.5), limed and unaffected soils demonstrated that N:S ratios were narrow when plants were grown on limed or unlimed sulfur-acidified soils, the plant P content was decreased by acidity and partially restored by liming, the Ca:Mg ratios were normal, and plant Mn levels varied with soil Mn.

The previous results prove conclusively that soils made barren by extreme soil acidity were not permanently sterile. That is, adequate applications of the proper form of lime readily counteracted soil toxicity and promoted good, normal plant growth.

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I. INTRODUCTION

The past decade has witnessed an upsurge of interest concerning the effect of modern civilization upon the environment. The idea of limitless resources has ended. Today, previous damage to the environment is being repaired. Also, numerous attempts are being made to find methods of reaping the benefits of modern technology without ruining our surroundings.

In Alberta, the majority of the natural gas contains significant quantities of hydrogen sulfide. For many years this "sour" gas was of little use as a fuel due to the sulfur content. In recent years (1950's) the process of removing the sulfur from the gas has been developed. This process has resulted in large amounts of usable natural gas and elemental sulfur. But the process of sulfur removal has caused certain problems concerning soil and water quality in the immediate vicinity of the natural gas processing plants. After the sulfur is removed from the gas it was previously poured into frames where it solidified into hard blocks. In order to transport sulfur by railway, the stockpile-sulfur was first ground to a powdered form, and then loaded into hopper cars. This grinding process was extremely dusty. If a wind was blowing at the time, considerable amounts of sulfur were carried downwind and deposited resulting in a serious soil acidity problem, due to oxidation of elemental sulfur

by microorganisms. Recently a "slating" process has been developed whereby sulfur is solidified into very small blocks which can be stored and transported without grinding. This process only partially reduced the sulfur dust problem and sulfur deposition on soil was still prevalent.

Due to the concern of Shell Canada towards the soil acidity problem, their gas plants at Innisfail and Waterton, Alberta, were selected as the sites at which to investigate this problem.

Preliminary studies (previous to the beginning of this investigation) at the Innisfail plant indicated that the neutralization of one sulfur-acidified soil with lime would restore plant growth to that soil. At Waterton, however, the acidity problem was more extensive and included soils with a range of pH values and levels of unreacted elemental sulfur.

Thus, the main objectives of this investigation were, to determine the form, amount, and placement of lime necessary to return plant growth to the sulfur-acidified areas at Waterton; and to determine the effect of acidity and liming on soil and plant chemical composition. A secondary objective was to determine the rate of soil acidification after sulfur application.

II. LITERATURE REVIEW

The purpose of this literature review is to investigate sulfur acidification problems similar to those found at Innisfail and Waterton, the reasons for acid soil infertility, the effects of liming acid soils, and the conditions and organisms responsible for sulfur acidified soils.

A. Soil Acidity Due to Sulfur Oxidation

1. Naturally occurring Sulfur-Acidified Soil:

The oxidation of reduced sulfur compounds has resulted in the formation of extremely acid soils in numerous coastal regions throughout the world. These soils are found mainly in tropical and subtropical coastal regions; such as Sierra Leone (Dent 1947, Hart 1959, Hart 1962, Jeffrey 1963), Suriname (Pons 1965), Indo China (Watt 1968), and Gambia (Evans 1966). Some countries in the temperate climatic zone have also experienced this problem. These include the Netherlands (Edelman and Van Staavern 1958), Japan (Murikami 1968), and the United States (Edelman and Van Staavern 1958, Fleming and Alexander 1961).

The acidified soils are commonly referred to as katteklies (cat-clays) or acid sulfate soils. Cat-clays form in tidal mangrove swamps, marshy backswamps of the seaward side of river deltas, or in lands that have been empoldered (Edelman and Van Staavern 1958, Moorman 1963).

The acid soils form when reduced sulfur compounds (pyrites, polysulfides, and elemental sulfur) are oxidized (Harmsen et al. 1954, Hart 1962, Quispel et al. 1952). These reduced sulfur compounds accumulate as the result of sulfates from the sea water being reduced by bacteria under waterlogged (anaerobic) conditions in the soil (Edelman and Van Staavern 1958, Fleming and Alexander 1961). This enrichment of the soil with sulfides may be enhanced by the translocation of sulfates from neighboring soils to a waterlogged (reducing) soil (Thornton and Giglioli 1965). The most common form of reduced sulfur which accumulates in these soils, is pyrites. This is due to the abundance of iron in most of the soils.

Under reducing conditions, the potential acid sulfate soils (cat-clays) are called "mud-clays" and have a pH value near neutrality (Edelman and Van Staavern 1958, Moorman 1963).

If the anaerobic environment ceases to exist due to drying of the soil, the reduced sulfur compounds begin to oxidize. As the soil dries (due to the onset of the dry season or empoldering and draining the land) the pyrites (and other polysulfides) oxidize to form ferric sulfate and sulfuric acid. The production of sulfuric acid lowers the soil pH value to a minimum of 2.0 to 2.5 (Edelman and Van Staavern 1958, Fleming and Alexander 1961, Hart 1959,

Murakami 1968).

It is generally agreed that the oxidation of polysulfides follows a two step mechanism. Firstly, there is a strictly chemical or autocatalytic decomposition of the least stable part of the soil polysulfide (Harmsen et al. 1954, Hart 1962). In the case of pyrites, the molecule chemically splits and the iron oxidizes and the sulfur accumulates in the elemental form (Quispel et al. 1952). Pyrites are stable at pH values near neutrality and quite reactive as the pH becomes more and more acidic. But some polysulfides are relatively unstable at neutrality. Thus, there is a rapid accumulation of small amounts of elemental sulfur immediately after the soil is aerated (Hart 1962). Since pyrites are considered to be unstable below pH 3.5 to 4.0, it was very puzzling to learn that some pyrites are relatively stable at pH 2.0 (Harmsen et al. 1954, Hart 1962). There are two hypotheses to explain this anomaly: (i) Pyrites exist in the soil as relatively insoluble particles of various size. Thus, small particles are readily oxidized and larger ones persist much longer (Hart 1962). (ii) Pyrite resistance to oxidation may be due to different proportions of phosphate to pyrites in some soils. Phosphates inhibit iron oxidation. Thus, high levels of phosphate may stabilize the pyrite molecule (Harmsen et al. 1954).

The second step in the production of sulfuric acid

from polysulfide oxidation is the microbial oxidation of accumulated elemental sulfur (Hart 1959). This second step catalyzes the first, and is limited in rate by the production of elemental sulfur by the first step (Hart 1962, Quispel et al. 1952). The organism responsible for the oxidation of elemental sulfur is Thiobacillus thiooxidans.

There are two sources, besides microbial oxidation, of the sulfates in cat-clay soils. These are: (i) translocation from surrounding areas by leaching or lateral diffusion, and (ii) accumulation of sulfates from a highly saline water table (Thornton and Giglioli 1965).

Another source of sulfuric acid is the basic ferric sulfate formed when the pyrite oxidizes. This molecule is unstable and slowly hydrolyzes, forming more acid in the process (Edelman and Van Staavern 1958).

The main effect of the extreme acidity is that of sterilizing the soil. The following are a number of factors contributing to soil sterility:

- (i) the very high hydrogen ion activity (Moorman 1963);
- (ii) the increase in the solubility and, thus, availability of potentially toxic ions. These include iron, aluminum, and manganese (Dent 1947, Evans 1966, Murakami 1968);

- (iii) decrease in availability of some essential nutrients such as phosphorus and nitrogen (Jeffery 1963, Murakami 1968, Watts 1968).

Cat-clay development may have an effect on the clay mineralogy of soils (Horn and Chapman 1968, Lynn and Whittig 1966). Under a reducing (mud-clay) environment, sulfide accumulation may cause interlayers to form in expandable 2:1 layer silicates. That is, chlorites may be synthesized. After oxidation and acid formation, the clay mineralogy remains unchanged for some years. But after sixty years clay minerals show general deterioration in crystallinity and chlorites show a marked destruction; probably altering to montmorillonite.

In managing mud-clays, two points of view have been expressed. Firstly, prevention of soil drainage so that aeration, and subsequent acid formation, does not occur. If this recommendation is adopted, these soils are useless for agriculture. It has been suggested that these areas of potential cat-clay formation should be set aside for such uses as wildlife refuges (Edelman and Van Staavern 1958). The second approach is to allow the soils to drain, and then reclaim them after acidification has taken place. The following methods have been used to reclaim acid sulfate soil areas in various parts of the world:

- (i) promote drainage to allow for rapid aeration

and acidification to occur. Over time, the toxins and acids will leach from the soil and eventually the soils will be useful for agriculture (Moorman 1963).

(ii) Liming and fertilization. The addition of liming materials and fertilizers has been widely used in reclaiming cat-clays. The effects of lime are the following: (a) stimulation of sulfur oxidation by raising the soil pH to a range favourable to Thiobacillus thiooxidans (Hart 1959).

(b) prevention of pyrite decomposition. Pyrite stability increases with a rise in soil pH (Hart, 1962).

(c) Decreasing toxic ion availability and increasing nutrient ion availability. Liming decreases available levels of such potentially toxic elements as Al, Fe, Mn, and H; and increases availability of nutrients such as phosphate (Tomlinson 1957, Shoop et al. 1961). All reports indicate that liming cat-clays to neutrality and heavy phosphate applications greatly improve the chemical status of these soils (Chenery 1954, Hart 1959, Murakami 1968).

When liming a sulfur-acidified soil there are two important factors to consider. Firstly, the lime application must be sufficient to neutralize the present acidity plus

that which will be produced due to sulfur oxidation stimulation. Secondly, the form of lime used must not raise the pH value to a point where plant growth is inhibited due to an alkaline soil pH (Hart 1959).

2. Sulfur Acidification due to Industry:

(a) Strip mining within a watershed in western Kentucky has produced enough acid water to significantly pollute the streams and groundwater, and produce extreme soil acidity. The oxidation of iron sulfides in the absence of calcium carbonate resulted in ferric sulfate and sulfuric acid production (Blevins et al. 1969, Kohnke 1950).

The acid caused an increase in solubility of such potentially toxic elements as iron, aluminum, manganese, zinc, lead, and arsenic. The high aluminum levels were the major plant limiting factor.

The addition of lime readily neutralized the aluminum acidity. Lime plus phosphorus, applied to the soil, greatly increased corn yields.

The recommendations for alleviation of the acidity were the following: (i) adequate drainage, (ii) reduction of further contamination by flood control measures and careful planning of further mining operations, (iii) adjustment of soil pH to 6.0 - 6.5 with lime, and (iv) supply phosphorus and other nutrients as deemed necessary.

(b) The removal of sulfur from natural gas resulted in deposition of elemental sulfur dust downwind from a gas processing plant near Innisfail, Alberta. Microbial oxidation of the soil-deposited sulfur acidified the soil to a point where plant growth was seriously inhibited (Nyborg and Schurer 1972). Soil pH was lowered to between 3.1 and 4.6 in a 3 acre area which had been barren for 5 or 6 years. Because the soil was barren, it was subject to erosion and much of the surface soil had been removed by water.

A preliminary greenhouse experiment indicated that liming the soil to neutrality with Ca(OH)_2 would restore a normal degree of plant growth to the sulfur-acidified soil. Subsequently, a field project was established to verify the greenhouse results. Plant growth on the limed acidified soil was very adequate but was not as great as on a normal soil in the same region. Underliming portions of the acidified area and low water infiltration on this eroded soil were presented as reasons for lower plant yields.

From this field project a full-scale reclamation of the acidified area was undertaken. Due to a wide variation in soil acidity it was inevitable that some of the area would receive excess lime and some would be underlimed. Thus, CaCO_3 was applied to the soil as excess amounts of this compound would be less harmful than over-liming with Ca(OH)_2 . Ca(OH)_2 may raise soil pH high enough to harm plant growth ($\text{pH} > 8$).

B. Acid Soil Toxicity to Plant Growth

The general infertility of soil observed as soil acidity increases is due to the increase in availability of certain toxic elements, the decrease in availability of some essential plant nutrients, and detrimental effects on certain microbial processes in the soil.

The major toxic effects of various elements arising in acidified soils are as follows:

- 1) Hydrogen ion toxicity (Jackson 1967). When only the hydrogen ion concentration is increased, there is general root damage when the pH value drops below 4.0 in the immediate root environment. That is, the toxicity is due to root tissue coming into direct contact with free inorganic acid of concentrations sufficient to damage living cells.
- 2) Manganese toxicity (Bortner 1935, Hale and Heintze 1946, Morris 1948). There is general agreement that decreases in soil pH are highly correlated with increased exchangeable and soluble manganese in soil; and with increased manganese in the plant. Plant injury is also well correlated with higher soil and plant manganese levels. A soil pH value of approximately 5.0 is the point where soil manganese levels become either harmful or harmless depending on whether soil acidity is increasing or decreasing. Plant sensitivity to manganese varies widely. Manganese toxicity symptoms were noted at tissue manganese levels of 1,000 ppm

in beans, 550 ppm in peas, and 200 ppm in barley. Manganese toxicity may be somewhat alleviated by additions of calcium or phosphate; but decreasing manganese availability is the only effective method of reducing toxicity.

3) Aluminum toxicity (Jones 1961, Magistad 1925, McLean and Gilbert 1928, Pierce and Stuart 1933). The solubility of aluminum increases somewhat as soil pH is lowered to approximately 4.5; then the solubility increases rapidly below this point. As the level of soluble aluminum increases, the amount in the plant increases correspondingly. The primary toxic effect of aluminum is the precipitation of phosphate, both in the soil and plant. This effect can be partially overcome by additions of superphosphate to the soil. As in the case of plant sensitivity to manganese, plant species vary widely in their tolerance to soluble aluminum. In some tolerant species, aluminum is taken into the plant, but the aluminum remains soluble even at neutrality. Thus, the plant can retain its phosphate status in the presence of aluminum levels detrimental to other species. It has been hypothesized that organic acids produced by the plant, act as chelating agents which prevent aluminum precipitation.

4) Other toxic elements:

(a) Copper (Olson et al. 1971) - There is an increase in solubility of copper compounds as the soil becomes more acid. Whether or not this is harmful to plants depends on

the total amount of copper in the soil.

(b) Zinc (Olsen et al. 1971) - Zinc toxicity only occurs where there are very high levels of zinc compounds in the soil.

The second major detrimental effect of soil acidity is deficiencies of certain elements resulting from lowering of the solubility and availability to these elements.

1) Calcium deficiency (Melsted 1953, Olson et al. 1971, Wallace and Hewitt 1948). It has been observed in corn and potatoes that a major reason for soil infertility at acid pH values is a lowering of plant available calcium, which is caused by high exchangeable and soluble aluminum levels. In general, when the pH is below 4.5 and exchangeable calcium is less than 2 me. per 100 g. of soil, the deficiency symptoms become apparent.

2) Phosphate deficiency (Birch 1951, Jackson 1969). There is wide agreement that decrease in plant available phosphate is a prime cause of acid soil infertility. As soil acidity increases there is a corresponding increase in both aluminum and iron oxide bound phosphate. Also, aluminum becomes the major cation on the exchange complex. This results in phosphate-aluminum-colloid linkages. All of these "bound" phosphates are quite unavailable to plants.

3) Molybdenum deficiency (Jones 1957). The behaviour of the molybdate ion, as soil acidity increases is analogous to that of the phosphate ion. The adsorption of molybdenum

by ferric and aluminum oxides, and clay colloids depends on soil pH and molybdenum concentration in solution.

4) Other deficient elements:

(a) Magnesium (Kamparth and Foy 1971). A low soil pH accompanied by high aluminum levels contributes to reduced magnesium uptake by plants.

(b) Potassium (Kamparth and Foy 1971). In general, very acid soils decrease potassium availability to plants.

The major microbial processes affected by soil acidity are symbiotic nitrogen fixation, and nitrogen, sulfur, and phosphorus mineralization (Jackson 1967, Kamparth and Foy 1971).

1) Symbiotic nitrogen fixation (Kamparth and Foy 1971)

(a) Microbial growth and survival: Rhizobia fail to grow well, if at all, in acid soils due directly to hydrogen ion effects. Poor growth may also be due to calcium and magnesium deficiencies in the acid soils.

(b) Nodulation: It is not clear whether poor nodulation is due to the direct effect of acidity (high hydrogen and aluminum activity) on the inoculation and nodulation process; or to a lack of viable organisms. However, to restore inoculation and nodulation in an acid soil, it is necessary to raise the pH plus supply calcium at levels greater than that required by the host plant.

(c) Nitrogen fixation: The restoration of a neutral

soil pH alone will not necessarily restore the nitrogen-fixing ability of legumes. Both the calcium and molybdenum requirements for nitrogen fixation are greater than the requirement of the host plant.

2) Mineralization of soil organic matter (Jackson 1967).

(a) Ammonification and Nitrification: The general trend is for ammonium to accumulate in soils of low pH. Since many organisms, with a wide range of acidity tolerance (e.g. fungi), have the ability to produce ammonium from organic matter, ammonification will occur at low soil pH. But the conversion of ammonium to nitrate is severely limited at pH values below 6.0. The abnormal proportions of ammonium and nitrate in acid soils may affect plant growth; as many species cannot efficiently use ammonium in acid conditions. The presence of ammonium (rather than nitrate) results in lowered calcium, magnesium, and manganese contents and increases phosphorus and chlorine contents in some plants.

(b) Sulfur mineralization: The mineralization rate of sulfur increases as acidity decreases. A three fold increase in sulfate production occurred after the pH of a soil was raised from 4.0 to 5.0. The release of plant available sulfur is limited by inhibition of organic matter breakdown under acid soil conditions.

(c) Phosphorus mineralization: Organic phosphorus mineralization increases with the soil pH. In acid soils, the most abundant organic phosphorus compounds are very

insoluble aluminum and iron phytates. Increasing soil pH generally causes mineralization of phytate phosphorus and, thus, more phosphorus becomes plant available.

(d) Organic matter mineralization and its effect on micronutrient release: There is evidence that microbe activity alters the solubility or oxidation states of manganese, zinc, copper, aluminum, iron, and molybdenum; and hence, toxicities and deficiencies are altered. Thus, soil pH variations which influence microbial activity will indirectly affect the activity of many elements in the soil.

C. The Effects of Liming Acid Soils

The effect of liming an acid soil largely benefits the nutrient status of the soil. This is accomplished by lowering the plant available levels of certain toxic elements (Al, H, Mn), by raising the availability of certain plant nutrients (P, Ca, Mo), and by restoring a favorable environment for most microbial activity. In the case of certain minor nutrients (Bo, Cu, Zn, Mn), liming may decrease their availabilities and plant deficiency symptoms may arise.

1) Liming Materials

In order to obtain the desired effects from liming an acid soil, there are a number of factors to consider pertaining to the liming materials to be used. These factors include form, fineness, and amount of liming

material applied to the soil.

The major forms of lime are calcitic (pure CaCO_3) and dolomitic ($\text{CaMg}(\text{CO}_3)_2$) limestone; and their corresponding hydrates ($\text{Ca}(\text{OH})_2$ and $\text{CaMg}(\text{OH})_4$), and oxides (CaO and CaMgO_2). Pure dolomite is comprised of 21.6 % Ca and 13.1 % Mg. In general, calcitic limestone is more rapid acting than dolomite, both chemically and biologically (Beacher et al. 1952, Beacher and Merkle 1949). Magnesium liming materials may be slightly more effective in soils which are very deficient in Mg (Crowther and Walker 1952). The hydrated lime forms are approximately the same as fine limestone (less than 200 mesh) in speed of action and effectiveness (Beacher and Merkle 1949). The oxides of calcium and magnesium are similar in effectiveness to ground limestone, of which 40 % will pass a 100 mesh seive (Crowther and Walker 1952).

The fineness of limestone greatly affects the ability of lime to neutralize the toxicity of acid soils. In general, coarse limestone is much less effective than finer lime in correcting all conditions that develop in an acid soil (Beacher et al. 1952, Crowther and Walker 1952, Hoyert and Axley 1952). Only extremely high rates of coarse lime (10 - 20 mesh) tend to gradually approach the effectiveness of 100 mesh limestone. Limestone which is less than 200 mesh is approximately as efficient as the

hydrated form; 100 - 200 mesh limestone is slower acting; and less than 20 mesh limestone is about $1/3$ as effective as hydrated lime (Beacher and Merkle 1949).

The amount of lime influences the amelioration of soil acidity problems (Beacher et al. 1952, Rixon and Sherman 1962). The satisfaction of the lime requirement of a soil by 100 % was as effective as adding 200 - 400 % of the lime requirement. Lime added at a rate of 50 % of requirement failed to inactivate the aluminum and manganese. When 400 % of the lime requirement was satisfied by hydrated lime, the pH was raised sufficiently high to cause plant yield reductions. Also, the "replaceable" phosphate was reduced when the pH rose above 7.4.

2) Effect of Placement on the Efficiency of Liming Materials

The incorporation of lime into the soil, by tillage equipment, is the most efficient method of neutralizing soil acidity (Barber 1967). In some instances, however, it may be desirable to apply the lime to the soil surface. For example, on grassland and in forested regions, lime cannot be incorporated into the soil without detriment to the vegetation.

A number of experiments have been carried out to determine the feasibility of neutralizing soil acidity at depth by surface applications of lime. For most soils a

minimum of 10 years is required for the neutralization of the top six inches of soil (Longnecker and Sprague 1940, Brown and Munsell 1936).

From the experiments on lime penetration reviewed, the following results and discussion were obtained:

1. Limestone and hydrated lime raised the pH sharply in the top four inches, 42 months after application. Hydrated lime was less effective as it caked and, thus, dissolved more slowly (Longnecker and Sprague 1940).
2. An application of CaCO_3 to the top six inches of soil, raised the pH significantly to a depth of 36 inches. This pH rise was realized 20 years after application.
3. Six years after a surface application of CaO the soil pH was raised slightly to a depth of nine inches. The greater part of the lime remained at the point of application (Nelson 1929).
4. A considerable length of time is necessary for a surface application of lime to penetrate to the sub-surface soil. In general, a surface application of lime does not affect the subsoil (Stewart and Wyatt 1919).

D. Organisms Involved in the Oxidation of Elemental Sulfur

There are a number of organisms which have the ability to form sulfates from reduced sulfur compounds. These organisms include heterotrophs, photo-autotrophs, and

chemo-autotrophs.

The most important organisms involved in the oxidation of sulfur compounds are the members of the species Thiobacilli. T. thioparus, T. denitrificans, and T. novellus are common in soils. T. thiooxidans and T. ferrooxidans are found only where there is considerable elemental sulfur and the reaction is acid (Starkey 1965). Because thiobacilli derive all of their energy from sulfur compounds, and because these substrates do not normally accumulate in soils, it would seem logical that thiobacilli should not be common to soils. There are two hypotheses to account for their presence: sulfur substrates are produced consistently but do not persist, or the bacteria are mutants of soil bacteria with less specific nutritional requirements (Starkey 1965).

T. thiooxidans principally oxidizes elemental sulfur or thiosulfate to yield energy. This species is extremely acid tolerant. It develops best at pH 2.0 - 3.0 and can produce 1.0 M sulfuric acid (Starkey 1965). The following physiological characteristics are common to T. thiooxidans:

1. Sulfur oxidation is most rapid in early stages of growth, then growth decreases as the production of H_2SO_4 increases (Li and Caldwell 1966).
2. The energy use efficiency decreases as the H_2SO_4 concentration increases (Starkey 1925).

3. Temperatures above 50°C are fatal. Optimum growth occurs between 27°C and 30°C. Oxidation is very slow when the temperature is less than 10°C (Li and Caldwell 1966).

4. The organisms are not resistant to desiccation and die out readily in the absence of moisture. Optimum oxidation is when moisture is at field capacity (Moser and Olson 1952, Attoe and Olson 1966).

The above characteristics of T. thiooxidans indicates that summer soil moisture and temperature conditions in Alberta will promote rapid oxidation of elemental sulfur deposited on the soil surface.

Thiobacillus thioparus is widely distributed in soils and grows best when pH is near neutrality. These organisms aerobically oxidize thiosulfate, sulfide, elemental sulfur, tetrathionate, and thiocyanate. Sulfate is the principal product, but some thiosulfate is also formed (Starkey 1950).

Thiobacillus ferrooxidans resembles T. thiooxidans as it is acid tolerant. This organism has the ability to use energy from aerobic oxidation of ferrous iron at acid reactions between pH 2.5 to 3.5 (Starkey 1965).

Thiobacilli spp. obtain all energy necessary for growth from the oxidation of inorganic sulfur compounds to

sulfate, and utilize CO_2 as the carbon source (Peck 1962).

For example, two energy producing reactions of T. thiooxidans are (Starkey 1925):



SUMMARY OF LITERATURE REVIEW

In many regions of the world, the oxidation of reduced sulfur compounds has resulted in serious soil acidification. The problem is largely alleviated by large applications of a suitable liming material.

Acid soil infertility is due to the increase in availability of toxic elements and the decrease in availability of nutrient elements as soil acidity increases.

The main beneficial effects of liming are to reverse the trends caused by a fall in soil pH. That is, toxic elements such as Al become unavailable and nutrients such as phosphates become more available.

The bacteria of the genus Thiobacillus readily oxidize reduced sulfur compounds under suitable soil moisture and temperature conditions. These organisms are capable of lowering a soil to pH 2.0 within a few weeks.

III. MATERIALS AND METHODS

INTRODUCTION

The soils used, for the most part, were obtained from the immediate regions of the Shell, Canada natural gas processing plants located near Waterton (figures 1 and 2) and Innisfail, Alberta. A description of each soil and the approximate sampling location are indicated in table 1 and figures 1 and 2. The letter assigned to each soil in table 1 will be used to designate that soil throughout the thesis. The various soil samples were air dried and ground to pass a 4 mesh sieve for greenhouse experiments and a 16 mesh sieve for all chemical analyses. The soil samples were used in greenhouse, incubation experiments, and for chemical analysis. The organic matter content of soils presented in Table 1 was determined from the total N level (N multiplied by 16) of the respective soils (Bremner 1965). Statistical tests performed on some greenhouse and field plot experiments were Analysis of Variance and Duncan's multiple range test (Steel and Torrie 1960).

The experiments conducted included two greenhouse projects comparing liming rates and forms; two incubations, one which compared liming forms and rates and the other determining the rate of soil acidification after sulfur application; four field plots at Waterton and two bush

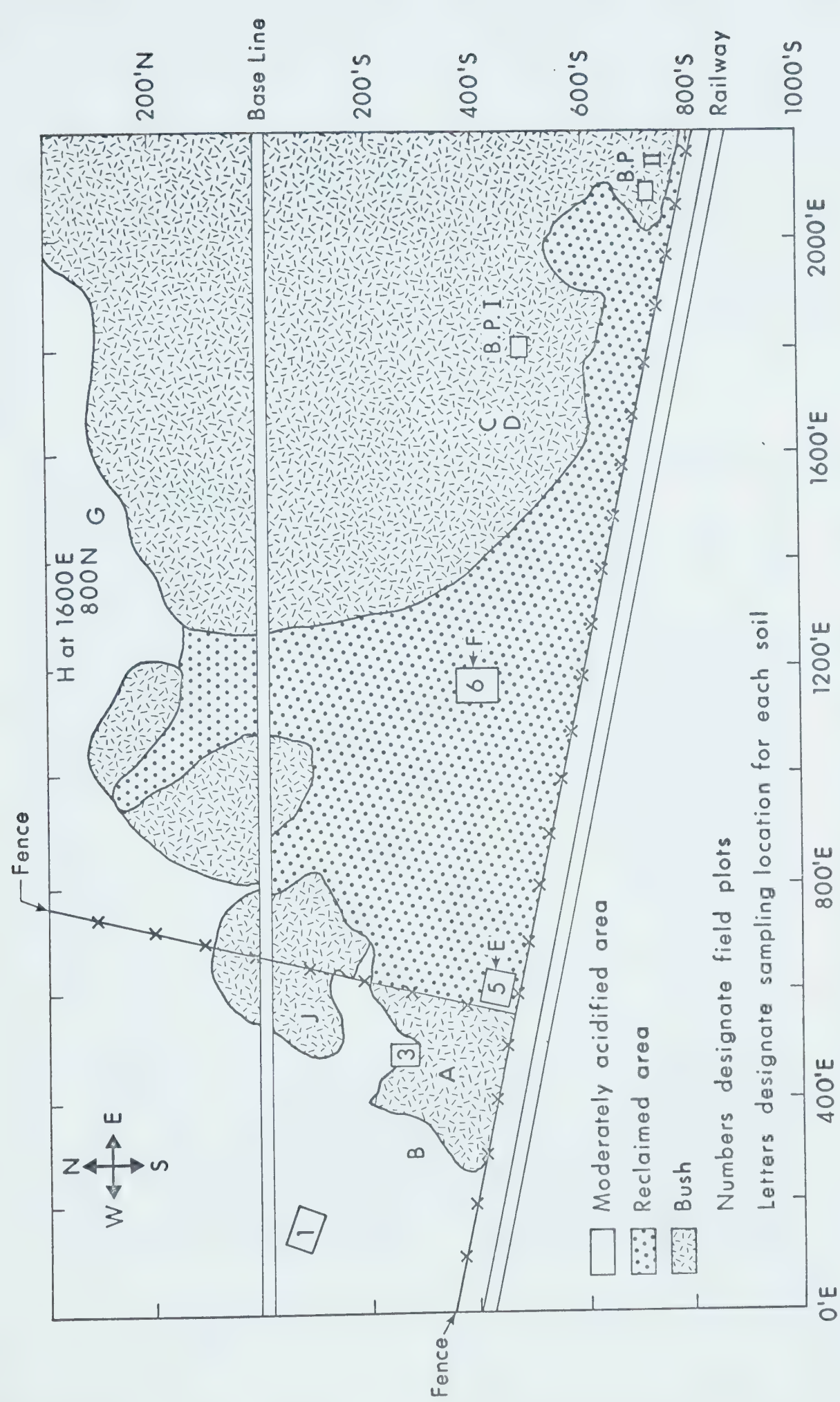


Figure 1: Reclaimed area, plot sites, and soil sampling locations at the Waterton gas plant.

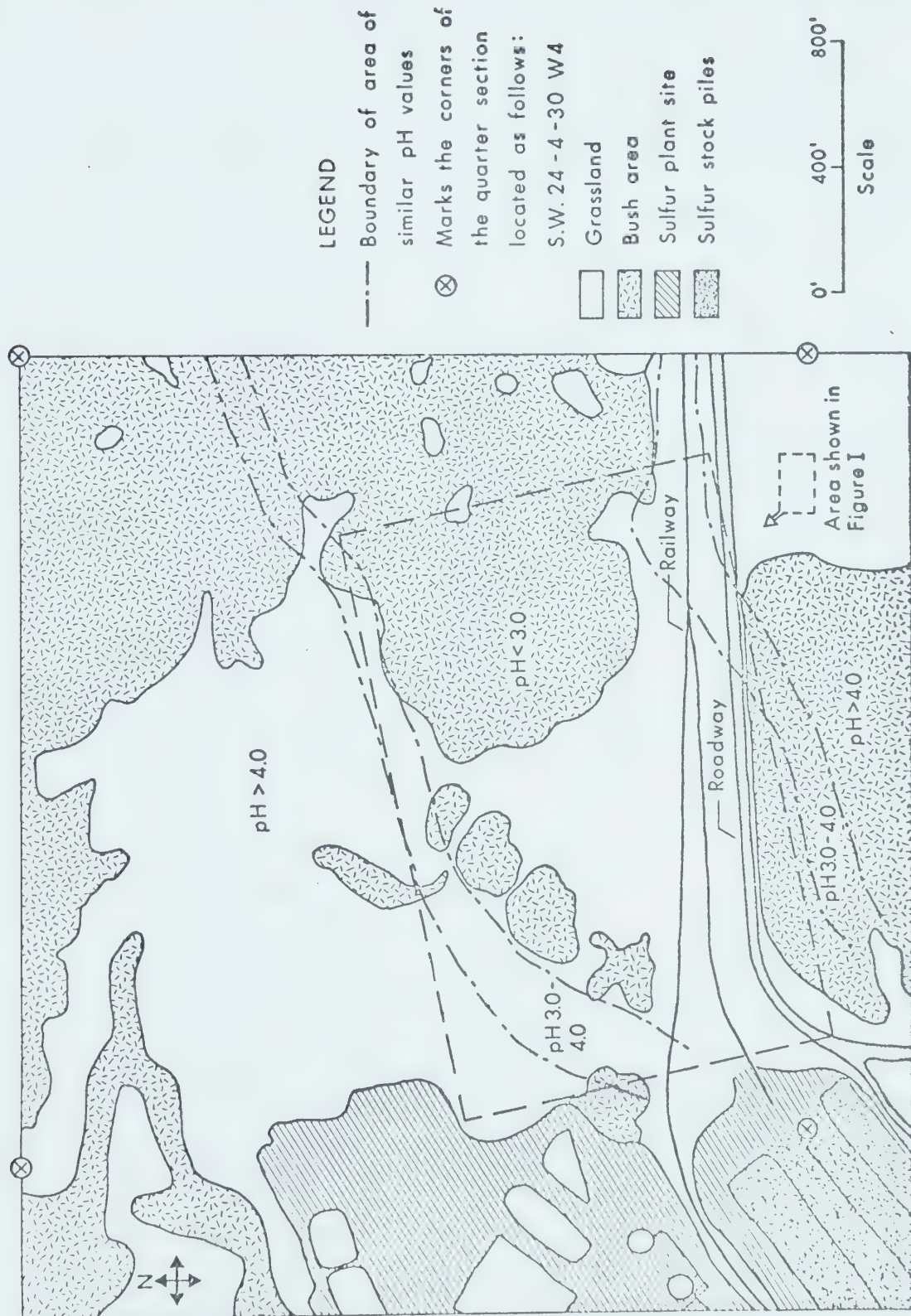


Figure 2: Plant site and sulfur-affected area at Waterton

Table 1. Description of soils used for greenhouse and laboratory experiments.

Soil	Location on figure 1	Original pH	Texture	O.M. %	Elemental S. content ppm
A	Waterton 400E, 400S	2.0	SL	2.2	600
B	Waterton 300E, 300S	3.6	SL	2.6	600
C	Waterton 1600E, 400S	0.9	L	5.2	1.7×10^4
D	Waterton 1600E, 400S	2.4	L	4.0	220
E	Waterton 600E, 400S	3.7	CL	0.84	10×10^3
F	Waterton 1200E, 400S	2.8	L	6.0	1.5×10^3
G	Waterton 1400E, 200N	3.5	SL	4.8	Nil
H	Waterton 1600E, 800N	4.6	SL	6.0	Nil
I	Waterton West of plant site	6.1	SL	8.4	Nil
J	Waterton 500E, 100S	2.1	L	3.0	1.0×10^4
K	Waterton	1.4	L	3.0	8.0×10^4
L	Innisfail South (nil)	3.0	L	2.6	Nil
M	Innisfail South (lime)	5.5	L	2.6	Nil
N	Innisfail (acidified area)	3.5	L	2.5	Nil
O	Innisfail	5.1	L	3.6	Nil
P	Innisfail (normal)	5.3	L	4.0	Nil
Q	Chernozem from near Calmar	5.9	L	7.0	Nil

plots at Waterton; laboratory projects to measure the downward movement of lime; chemical analysis of limed and unlimed soils; and the determination of the chemical composition of plants grown on acidified, limed, and unaffected soils.

A. Greenhouse and Incubation Experiments

1. A Comparison of $\text{Ca}(\text{OH})_2$ and CaCO_3 Applications on Two Sulfur-Acidified Soils (Soils A and B).

The first greenhouse and incubation experiments were undertaken to determine the effect of $\text{Ca}(\text{OH})_2$ versus CaCO_3 on soil pH, elemental sulfur oxidation, and plant growth. The soils used were A and B. Soil A was a sandy loam having an original pH of 2.0, containing 2.2% organic matter, and had an unreacted elemental sulfur level of 600 ppm (Table 1). Soil B was very similar to soil A as to organic matter content, texture, and sulfur level, but was less severely acidified (pH 3.6).

The experiments were arranged in a Randomized Complete Block design, with 6 replicates and 7 treatments for each soil. In the greenhouse, 1400 g. of soil were weighed into each pot. One hundred g. of soil were weighed into 150 ml. erlenmeyer flasks in preparation for incubation at 22°C.

The treatments were three rates each of CaCO_3 and $\text{Ca}(\text{OH})_2$, plus a control for each replicate. The lime required for Soils A and B was determined by measuring soil

pH after the soil was equilibrated for three days with serial additions of Ca(OH)_2 and CaCO_3 . The lime additions were thoroughly mixed with 20 g. of soil and to this mixture was added 50 ml. of water. The amount of lime which neutralized the soil was converted to parts/million and then to tons/acre assuming that one acre of soil weighs 2 million lbs. This amount of lime was considered to be the lime requirement for that soil. The first treatment of lime added to soils A and B was the lime requirement rate. The second rate was twice the lime requirement; and the third rate was four times the lime requirement. The treatment rates for soil A were equivalent to 15 tons per acre, 30 tons per acre, and 60 tons per acre of Ca(OH)_2 ; and 20.3 tons per acre, 40.6 tons per acre, and 81.2 tons per acre of CaCO_3 . The treatments for soil B were 15, 10, and 20 tons per acre of Ca(OH)_2 and 6.5, 13, and 26 tons per acre of CaCO_3 . The corresponding treatments of Ca(OH)_2 and CaCO_3 were chemically equivalent as to the amount of Ca added.

(a) Effect of lime on plant growth in greenhouse:

In the greenhouse, both Soils A and B were cropped twice. Four species of plant were grown on each soil when they were first cropped. On soil A, Fairway Crested Wheat and Carlton Brome grass were seeded in each treatment of three replicates. Climax Timothy and Olds Creeping Red Fescue were planted on the other three replicates. That is, two species of grasses were sown in each pot. Approximately 30 seeds of each grass were planted. On Soil B, Carlton

Brome and Olds Creeping Red Fescue were planted in each pot on three replicates, and Ladak Alfalfa and Pendek Oats were seeded on the other replicates. Ten seeds of oats and 30 seeds of the other plant species were planted in each pot.

Before seeding, each pot of soil was fertilized with 100 ppm of N as NH_4NO_3 and 40 ppm of P as KH_2PO_4 . Nitrogen was reapplied as a top dressing after each cutting of the plants.

The plants were counted upon emergence, and then harvested at 6 week intervals, for a total of 3 cuttings on Soil A and 2 cuttings (only 1 cutting for oats) on Soil B. Dry weight plant yields were measured for all treatments.

Oats and Galt Barley were seeded on both Soils A and B for the second cropping. Oats were seeded (10 seeds) on three replicates and Barley (10 seeds) on the other three. The plants were counted upon emergence and, then, harvested after 6 weeks and the dry weight yields measured.

(b) Effect of lime on pH and elemental sulfur content of the soil:

The incubation experiment was designed to monitor soil pH and elemental sulfur content over an extended period of time. The soils were maintained near field capacity and the temperature held constant at 22°C. The pH of both soils

A and B were measured at intervals of 0, 3, 9, 27, 81, and 273 days. One of the six replicates on each soil was used at each date of measurement. Elemental sulfur was measured only on soil A as the initial sulfur contents of both soils were equal.

The soil pH measurement was obtained using a 2.5:1 water to soil ratio (Peech 1965). The elemental sulfur was measured using a modification of the Hart method (Appendix VII).

The greenhouse soils were sampled at cutting time during the first cropping, and before and after the second cropping. The soil pH was measured on all soils, while elemental sulfur was measured only on the Soil A samples obtained during first cropping.

2. Comparison of CaCO_3 and MgCO_3 Applications on Two Acidified Soils (Soils J and K):

The second greenhouse experiment was designed to determine the effect of CaCO_3 versus MgCO_3 on soil pH, electrical conductivity, and plant growth. The soils were two medium textured soils having an extremely acid pH and a very high level of elemental sulfur.

The experiment was arranged in a Randomized Block design with 8 treatments and 3 replicates for each soil. The lime was added to 500 g. of soil, in each pot, at a rate of 10 per cent (50 g.) of the soil weight. The seven liming treatments were comprised of various combinations of CaCO_3 and MgCO_3 , ranging from 100 per cent CaCO_3 to 100 per cent MgCO_3 .

(a) Effect of Lime on Plant Growth:

Pendek Oats were seeded, at a rate of 12 seeds per pot, in each treatment. The soils were fertilized with 100 ppm of N (as NH_4NO_3) and 40 ppm of P (as KH_2PO_4).

A number of plant emergence counts were taken to observe the effect of lime form on plant germination and emergence. The oats were harvested after $3\frac{1}{2}$ weeks of growth, and dry weight yields were determined.

(b) Effect of Lime on pH and Electrical Conductivity:

After the oats were harvested, the soils were dried and sieved. A saturated soil paste extract was obtained from each treatment. The soil pH and electrical conductivity of the extracts were measured (Bower and Wilcox 1965).

3. Comparison of the Effects of Elemental Sulfur Applications on Acidified, Limed, and Unaffected Soils (Soils A, L, M, and Q).

The second incubation experiment was designed so as to observe the effect of elemental sulfur application upon soil pH of four soils of widely varying acidity. Also, the rate of elemental sulfur oxidation within the four soils was to be measured. Soil A was a very acidic soil from Waterton. Soils L, M were unlimed and limed soils from the

plots at Innisfail. Soil Q was an unaffected Black Chernozem from near Calmar Alberta.

Elemental sulfur was applied at a rate of 1 per cent of the soil weight to 100 g. of each soil. Four 100 g. samples of the four soils were weighed into 125 ml. erlenmeyer flasks. The treatments consisted of two nil treatments and two of sulfur. The soils were incubated at 22°C for periods of 0, 3, 6, and 12 weeks. The soil moisture content was maintained near field capacity.

After each incubation period, the soil pH and elemental sulfur content were measured as in the first incubation experiment.

B. Waterton Field Plot Experiments

In order to verify the results obtained from the greenhouse and incubation projects, four field plots were set up in the region east of the gas plant site (figure 1). The plot sites were distributed throughout the acidified area so as to encompass most variations in soil pH, elemental sulfur content, soil texture, and topography in this area.

The plots were arranged in Split Plot Design .
The plots were limed with a surface application of

the desired rate. The lime was then mixed to a depth of 6 inches with a rototiller. Before seeding the plots, each received mineral fertilizers at the rates of 100 pounds per acre of N, P and K, as 35-0-0, 0-45-0, and 0-0-60, respectively. The various crops planted were either broadcast, followed by a light rototilling, or drilled into the soil with a single share hoe drill.

During the growing season of 1972, plots 1, 5, and 6 were watered in order to prevent plant stress due to lack of moisture.

The plots were harvested in September of 1972, before the plants had reached full maturity. Two, 10 foot rows of each plant species were sampled where possible. The samples were dried and a dry weight yield for each replicate of each treatment was obtained.

The following is a more detailed description of each plot:

1) Plot 1:

The first plot (figure 1) was established in the autumn of 1971, on a sandy hill near the eastern boundary of the gas plant site. The plot dimensions were 68 ft. x 55 ft. Plot 1 consisted of 6 treatments and two replicates.

Lime was applied at the following rates: 5 tons/acre and 10 tons/acre Ca(OH)_2 , and 6.5 tons/acre, 13 tons/acre,

and 19.5 tons/acre CaCO_3 . Each treatment subplot measured 20 ft. x 10 ft.

Carleton Brome, Pendek Oats, and Ladak Alfalfa were seeded by hoe drill at rates of 10, 60, and 10 pounds per acre, respectively. The crops were seeded in rows nine inches apart. During the growing season, plot 1 was watered periodically to promote healthy plant growth.

2) Plot 3:

Plot 3 was also limed in the fall of 1971. The plot was located on an eastward facing slope approximately 400 ft. east of the plot 1 site (figure 1).

The plot measured 55 ft. x 50 ft. and consisted of 4 treatments and two replicates.

The liming rates were 10 tons/acre, 20 tons/acre, and 10 tons over 5.5 tons per acre of Ca(OH)_2 . The latter treatment was accomplished by removing the top 6 inches of soil and then liming the 6 to 12 inch depth with 5.5 tons/acre. The surface 6 inches of soil was then replaced and subsequently limed at a rate of 10 tons/acre. This treatment was designed to indicate whether or not a lime application to a depth of 12 inches promoted an increase in growth over lime applied only to the surface 6 inches.

The dimensions of the treatment sub-plots were 20 ft. x 10 ft.

Carlton Brome, Galt Barley and Reed Canary Grass were seeded by hoe drill at rates of 10, 60, and 10 pounds per acre respectively. The crops were seeded with a nine inch spacing. Each plant species occupied one third of each treatment sub-plot.

3) Plot 5:

Plot 5 was established in the spring of 1972. The plot site was on nearly level ground near the southern boundary of the acidified area (figure 1). The soil had been disturbed by heavy equipment and was a mixture of heavy textured sub soil and loam textured surface soil. The plot was downslope from a wooded region. Thus, it was protected from elemental sulfur deposition, but received the acid water run-off from the wooded area.

The plot dimensions were 60 ft. x 60 ft. and consisted of 5 treatments and 4 replicates. The liming treatments were 2 tons/acre, 6 tons/acre, 10 tons/acre, and 24 tons/acre of CaCO_3 . The treatment sub-plots measured 12 ft. x 15 ft.

Plot 5 was first seeded by broadcasting a mixture of Reed Canary Grass, Ladak Alfalfa, Carlton Brome, Olds Creeping Red Fescue, and Climax Timothy. The seeding rate was approximately 10 pounds per acre of each crop. Pendek Oats was then drilled into the soil at a rate of 60 pounds per acre. The oats were seeded in rows at intervals of one foot. Thus, 12 rows of oats were seeded on each treatment.

Plot 5 was also watered periodically during the growing season.

4) Plot 6:

Plot 6 was also started in the spring of 1972. The plot was located near the lowest topographical point of the acidified region. The soil was a loam in texture and high in organic matter content (about 6.0 - 7.0 per cent). The plot dimensions were 60 ft. x 60 ft. and consisted of 4 treatments (nil, and 4, 13.5, and 29 tons/acre of CaCO_3) and 4 replicates. Each treatment of plot 6 was seeded to Pendek Oats, Galt Barley, Reed Canary Grass, Carlton Brome, Climax Timothy, and Olds Creeping Red Fescue. The grasses were sown at a rate of 10 pounds per acre and the cereals at a rate of 60 pounds per acre. Each crop, occupying one sixth of a treatment, was sown by hoe drill with a nine inch spacing between each row.

From the data obtained from the Waterton plots, a reclamation plan for the sulfur-acidified region was formulated.

C. Downward Movement of Lime

The investigation of neutralization of soil acidity at depths below the application region, was a second purpose of the Waterton plots. In conjunction with this study, the

neutralization of soil acidity in forested soils was also investigated.

1. Downward Movement of Lime on the Waterton Field Plots:

The acidity at the Waterton gas plant site extended to depths of three feet or more. That is, over time the acidity produced at the surface had leached downward, significantly lowering the soil pH a depth. Since economics prevented the application of lime to a depth lower than 6 inches, it was desirable to learn whether or not surface liming would eventually neutralize the acidified subsoil.

During the growing season of 1972, the Waterton plots were sampled extensively in order to determine the soil pH at various depths. In general, the soils were sampled at 0-6 in., 6-8 in., 8-10 in., and 10-12 in. depths. The pH values were determined on each replicate of each treatment.

2. Downward Movement of Lime on Bush Soils¹:

Since trees provided a wind break and, thus prevented extensive spreading of the sulfur, it was deemed desirable

¹ Bush soils designates soil located in regions of poplar growth at the Waterton plant site.

to neutralize the acid bush soils without removal of the trees. Although the trees were dying, surface applications of lime were considered as a method of neutralizing the soil, at depth, and preventing loss of the trees. In order to evaluate the feasibility of this reclamation method, the following projects were undertaken:

(a) Waterton Bush Plots (figure 1):

Bush plot 1 was situated on an extremely acid area near a slough and in a very moist environment. Bush plot 2 was situated on a sandy hill of moderate acidity.

The plots consisted of two treatments and two replicates. The treatments were 20 tons/acre $\text{Ca}(\text{OH})_2$ and CaCO_3 . The lime was spread on the soil surface and mixed with the top inch of soil. The plot dimensions were 10 ft. by 7 ft.

The plots were sampled at depths of 0-1 in., 1-2 in., and 2-4 in. The pH values of each treatment and control samples were determined in order to observe whether or not the lime had moved downward.

(b) Greenhouse Box Experiment:

Further investigation of the neutralization of bush soils was undertaken in the greenhouse. Soils C and D were used for this experiment. Soil C was the extremely acid, high sulfur content, surface soil from the bush. Soil D was the less affected subsoil from the bush. This experiment was designed to observe the effect of surface liming on

subsoil pH values, the effect of removal of the surface soil on subsoil neutralization, and the effect of surface liming on plant growth.

The soils were weighed into 7.5 inch deep plywood boxes. Four boxes contained a 5 inch depth of soil D topped by 1 inch of soil C. These boxes attempted to simulate bush soil in the undisturbed state. The other four boxes contained only soil D to a level of 6 inches. Thus, there were four boxes of intact bush soil and four of bush soil with the sulfur-containing surface soil removed. Each soil received a 20 tons/acre application of CaCO_3 to the surface inch of the soil in two of the boxes. The other two boxes (of each soil) were left as controls.

Each box was seeded to Pendek Oats (16 seeds per box), Ladak Alfalfa (10 lb./ac.) and Climax Timothy (10 lb./ac.). The soils were fertilized at a rate of 50 lb./ac. of $\text{N}(\text{NH}_4\text{NO}_3)$ and 50 lb./ac. of $\text{P}(\text{KH}_2\text{PO}_4)$. The moisture level of each soil was kept near field capacity. Over the 6 week duration of the experiment, each soil received a total of 3.2 inches of water.

The soil was sampled twice during the course of the experiment. The sampling depths were 0-1 in., 1-2 in., and 2-6 in. The oats were harvested and a dry weight yield was obtained.

(c) Laboratory Tube Experiment:

A similar experiment to the box experiment was undertaken in the laboratory. Twelve plastic tubes (1-2 in. in diameter) were filled with 7 inches of bush soil. Six tubes contained 6 inches of soil D topped by 1 inch of Soil C. The other tubes contained 7 inches of soil D. Thus, the soils were the same as for the box experiment. Two of the intact soils and two soils with the surface removed were limed with 20 tons/acre CaCO_3 . The same number of tubes received 20 tons/acre $\text{Ca}(\text{OH})_2$. The other four tubes (2 of each soil) were left as controls. The lime was thoroughly mixed with the surface inch of soil.

The experiment was performed over a two week period. During that time the soils received an application of 1 inch of water each day for a total of 14 inches. The soils were then removed from the tubes and the pH values were measured on each inch of each soil. That is, a total of 7 pH determinations were performed on each soil.

D. Chemical Analysis of Acidified, Limed, and Unaffected Soils.

A number of soils from Waterton and Innisfail were analysed in order to observe the effect of soil acidification and subsequent liming on the chemistry of the soils. Also, two unaffected soils were analysed so that a comparison between normal, acidified, and limed soils could be made.

1. Effect of CaCO_3 and Incubation on the Chemistry of Acidified and Unaffected Soils:

Eleven soils (A, B, D, E, F, G, H, I, N, O, and P) were limed and incubated in order to observe the effect of liming on various chemical components of the soils. The selected soils vary widely in original pH, texture, organic matter, and location. Soils A, B, D, E (plot 5), and F (plot 6) were very acid soils from Waterton. Soils G and H were less severely affected soils from Waterton. Soil I was an unaffected soil from west of the Waterton plant site. Soil N and O were an acidified and a nearly unaffected soil from Innisfail. Soil P was a normal soil from near the Innisfail plant site.

Four 100 g. samples of each soil were incubated for six weeks at 22°C . Two of the samples were limed at a rate necessary to bring the soil pH to 6.5 plus compensate for potential acidity due to elemental sulfur oxidation. The other two samples were controls. The soils were maintained at field capacity throughout the incubation period.

After incubation the soils were dried and sieved. The following chemical analyses were performed on both incubated soils and an unincubated sample of each of the soils:

- i) Ammonium and nitrate N were determined by steam distillation (Bremner 1965).
- ii) Phosphate was measured by the Miller and Axley (1956) method.

iii) Sulfate was measured by the Johnson and Nishita (1952) method. The soil was extracted with water using a 2:1 water to soil ratio.

iv) Extractable¹ K, Ca, Mg, Na, Al, and Mn were measured by atomic absorption spectroscopy. The soils were extracted in a 1:5 soil to solution ratio. K was extracted in N NH_4Cl and the other ions were extracted in N KCl.

2. Effect of Various Rates of Ca(OH)_2 and CaCO_3 on the Chemistry of Acidified Soils (Soils A and B):

After the final cropping of soils A and B (first greenhouse experiment), the soil treatments were combined and retained for further analysis. All treatments of both soils were analysed for NH_4 , NO_3 , available P, sulfate, K, Ca, Mg, Na, Al, and Mn. The methods employed were the same as used in the previous analysis.

3. Chemical Analysis of Plot 6 Soils:

The soil samples of plot 6, obtained in the autumn of 1972, were analysed in the same manner as the incubated and greenhouse soils. The surface 6 inches of each replicate of each treatment were analysed.

E. Analysis of the Chemical Composition of Oats and Barley Grown on Acidified and Limed Soils

The analyses were performed on plant samples obtained

¹ Extractable denotes easily soluble plus exchangeable ions.

from two greenhouse experiments, two plots at Waterton, and two plots at Innisfail.

Digestion of Plant Material for Mineral Analysis:

The dried plant samples were ground to pass a 20 mesh seive. Total N was determined by the semi-micro Kjeldahl method (Bremner 1965). The remaining chemical parameters, except for total sulfur, were determined on a diluted dry ash sample of the plant material. A 0.2 g. or 0.5 g. sample was ashed in a muffle furnace at a temperature of 485°C for a period of four hours. The resulting ash was dissolved in 2N HCl and diluted with water to a 25 ml. volume. The following chemical analyses were then performed on the diluted HCl extract:

- i) Total phosphorus was determined using the ascorbic acid - H_2SO_4 color developing solution of the Miller and Axley soil phosphate method. A 0.5 ml. aliquot of the plant extract was added to a 50 ml. volumetric flask, along with 10 ml. of the color developing solution. Total phosphate was then determined by following the Miller and Axley (1956) method.
- ii) Total K, Ca, Mg, Na, Al, Mn, Zn, and Fe were determined by the use of atomic absorption spectroscopy (Isaac and Kerber 1971).

The total sulfur content of the plant material was determined from a diluted wet ashing of plant material. A 0.5 g. sample was wet ashed using the nitric-perchloric acid method. The total sulfur content was then measured by the Johnson and Nishita (1952) method.

1. Chemical Analysis of Plants Grown in the Greenhouse:

(a) Comparison of Oats grown on Soils A and B.

The oats grown on soils A and B during the second cropping of the first greenhouse experiment were analysed as previously indicated. The entire dried oat plants were combined by treatments and ground to pass a 20 mesh seive. Two 0.2 g. samples from each treatment were used for both the micro-Kjeldahl and dry ashing procedures.

(b) Comparison of Barley grown on Soils I and K.

The other greenhouse experiment, from which plant samples were obtained for analysis, was one involving extremely high rates of CaCO_3 addition to an acidified and a normal soil. The acidified soil (K) was of extremely low pH and had a very high level of elemental sulfur. The normal soil (I) was obtained from west of the Waterton plant site. The liming rates of soil K were 4.2 per cent, 14.6 per cent, and 58.2 per cent of the soil weight. The rates for soil I were nil, 14.6 per cent, and 58.2 per cent of the soil weight. The barley obtained from this experiment was combined by treatment and two 0.2 g. samples, from each treatment, were analysed as previously indicated.

2. Chemical Analysis of Oats Grown on Waterton Plots 1 and 6:

The whole oat plants sampled from the fertilized treatments of plot 1 and from plot 6 were used for analysis. A 0.5 g. sample from each replicate of each treatment was

used for the micro-Kjeldahl, the dry ashing and wet ashing procedures.

3. Chemical Analysis of Oat Seed Grown on Innisfail Plots North and South:

Only the oat seed obtained from the Innisfail plots was analysed. The seed was ground, as for previous analyses, and a 0.5 g. sample from each replicate of the nil and lime treatments was analysed.

IV. RESULTS AND DISCUSSION

INTRODUCTION

The various experiments undertaken will be discussed under the same headings as used in the Materials and Methods section.

For the experiments concerning liming rates and forms, the relative merits of each form and rate will be discussed and conclusions drawn as to the liming procedure best suited to alleviating the acidity problem. Following this, the feasibility of neutralizing sub-surface acidity by surface lime applications will be discussed. Finally, a general discussion as to the effect of acidity and liming on soil and plant chemistry will conclude this section.

A. Greenhouse and Incubation Experiments

To determine the amount of lime necessary to neutralize a sulfur-acidified soil, each soil was equilibrated with a range of $\text{Ca}(\text{OH})_2$ additions for three days. After equilibration, the soil pH values were determined. The amount of lime which raised the soil pH to neutrality was deemed the lime requirement for that soil. Table 2 shows the $\text{Ca}(\text{OH})_2$ ranges and resultant pH values for the lime requirement determination for 4 acidified Waterton soils. The lime requirement was determined for the 0-6 in. and 6 in. to 12 in. depths for each soil.

Table 2. Lime requirement of four sulfur-acidified soils from Waterton.

Treatment	Depth	pH	
		Soil 1	Soil 2
Nil	0-6"	2.4	2.9
10 tons/acre	Ca(OH) ₂	3.9	5.4
15 tons/acre		5.0	6.5
20 tons/acre		6.2	8.0
Nil	6"-12"	2.9	3.8
5 tons/acre	Ca(OH) ₂	3.7	5.6
10 tons/acre		5.0	7.2
20 tons/acre		6.2	8.5

Treatment	Depth	pH	
		Soil 3	Soil 4
Nil	0-6"	3.6	3.5
2.5 tons/acre	Ca(OH) ₂	4.0	4.3
5 tons/acre		4.5	5.1
10 tons/acre		6.0	6.5
Nil	6"-12"	3.7	4.4
1.25 tons/acre	Ca(OH) ₂	3.9	5.0
2.5 tons/acre		4.2	5.7
5 tons/acre		4.9	6.8
10 tons/acre	Ca(OH) ₂	6.3	8.2

1. Comparison of $\text{Ca}(\text{OH})_2$ and CaCO_3 Applications on Two Sulfur-Acidified Soils (A and B):

Two sulfur-acidified soils from Waterton were limed with various rates of $\text{Ca}(\text{OH})_2$ and CaCO_3 to determine the effect of lime rate and form on soil pH, elemental sulfur oxidation, and plant growth. The soils used for both the greenhouse and incubation experiments were soils A (pH 2.0) and B (pH 3.6). Both soils were sandy loam in texture and contained about 600 ppm elemental sulfur.

For the greenhouse and incubation experiments, the soils received the same treatments. That is, for soil A the liming rates were 15, 30, and 60 tons per acre of $\text{Ca}(\text{OH})_2$; and 6.5, 13, and 26 tons per acre of CaCO_3 . The corresponding treatments of $\text{Ca}(\text{OH})_2$ and CaCO_3 were at chemically equivalent rates as to the amount of Ca (e.g. 60 tons/acre $\text{Ca}(\text{OH})_2$ and 81.2 tons/acre CaCO_3 are equivalent).

The incubation experiment was undertaken in order to complement the greenhouse experiment. That is, the purpose of incubating the soils was to determine the effect of liming on soil pH and elemental sulfur oxidation over an extended period of time (243 days) under controlled conditions.

(a) Effect of Lime on pH and Elemental Sulfur Content:

Liming an acid soil (A) raised the pH to neutrality or above, and stimulated S oxidation (Table 3,

Fig. 3, 4 and Appendix I). In the greenhouse experiment S oxidation was stimulated to a greater extent by 20.3 tons/acre CaCO_3 than by 81.2 tons/acre; however, the reverse was observed in the incubation experiment. Initially, CaCO_3 raised the pH to values conducive to optimum plant growth, regardless of rate. But over time the low liming rate (20.3 tons/acre) was significantly decreased in pH due to stimulation of elemental sulfur oxidation (figure 3 and appendix I). The two higher rates of CaCO_3 (40.6 and 81.2 tons/acre), however, maintained the soil pH near neutrality. These rates of CaCO_3 were twice and four times the amount necessary to neutralize the present acidity of soil A.

On the other hand, Ca(OH)_2 only neutralized the soil when applied at a rate of 15 tons/acre, which was the lime requirement for soil A. A 30 tons/acre application raised the pH above 8.0, while a 60 tons/acre application raised the pH above 10.0.

Over time the soil pH was lowered on all treatments but nil, and 40.6 and 81.2 tons/acre of CaCO_3 . This indicates the stimulation of elemental sulfur oxidation as the soil pH was raised (figures 3 & 4). The treatments in which liming rates merely compensated for present acidity (15 tons/acre Ca(OH)_2 and 20.3 tons/acre CaCO_3) were lowered to pH 5.0 or below. That is, the soil acidity was increasing, again, to a point where plant growth may be harmed. The pH of the

Table 3. Effect of amount and form of lime on changes in pH and elemental sulfur content of soil A (greenhouse).

Treatment	First Cropping					Second Cropping	
	6 weeks		12 weeks		18 weeks		pH after harvest
	pH*	Sulfur *	pH	Sulfur	pH	Sulfur	
Nil	2.3f**	538	2.2f	637	2.2e	622	2.4
15 tons/acre Ca(OH) ₂	6.0e	516	5.5e	427	5.0d	277	4.6
30 tons/acre Ca(OH) ₂	8.2b	510	8.1b	563	7.9b	472	7.5
60 tons/acre Ca(OH) ₂	10.5a	607	10.1a	585	9.6a	610	8.1
20.3 tons/acre CaCO ₃	6.3d	506	5.8d	397	5.1d	237	5.0
40.6 tons/acre CaCO ₃	7.3c	510	7.4c	440	7.3c	284	7.2
81.2 tons/acre CaCO ₃	7.3c	457	7.4c	522	7.5c	346	7.3

* Original pH 2.1; original sulfur 600 ppm.

** Treatment results not followed by the same letter are considered significantly different at the 1% level.

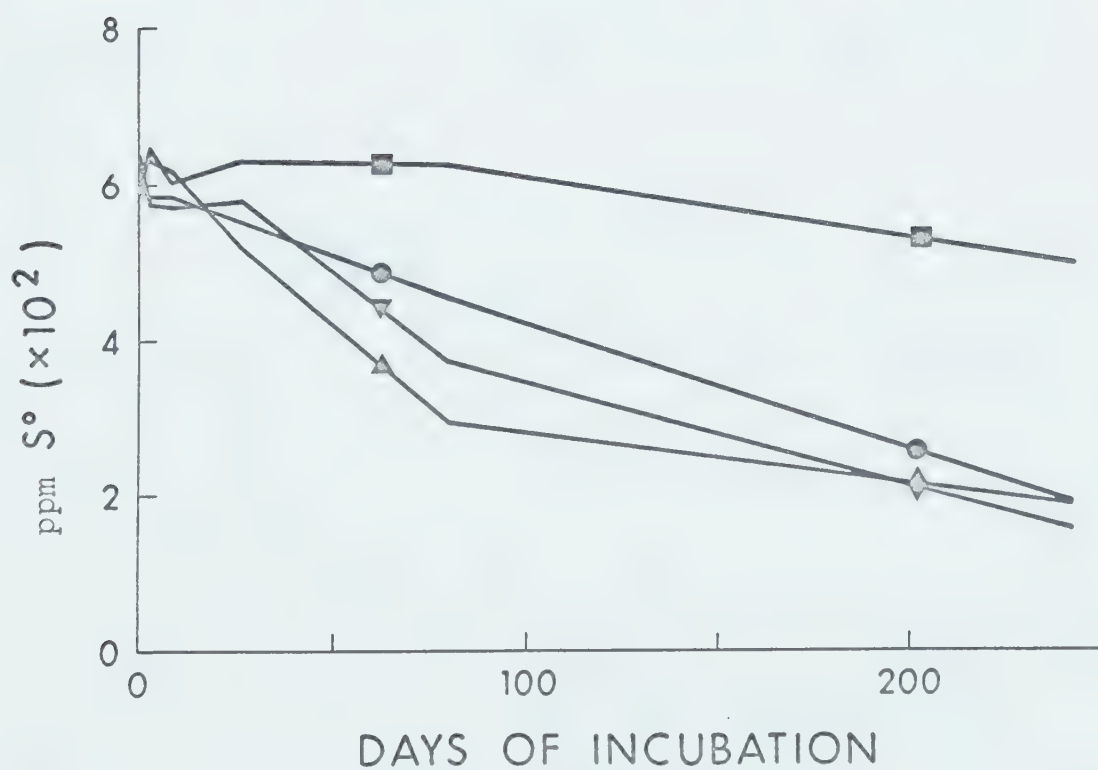
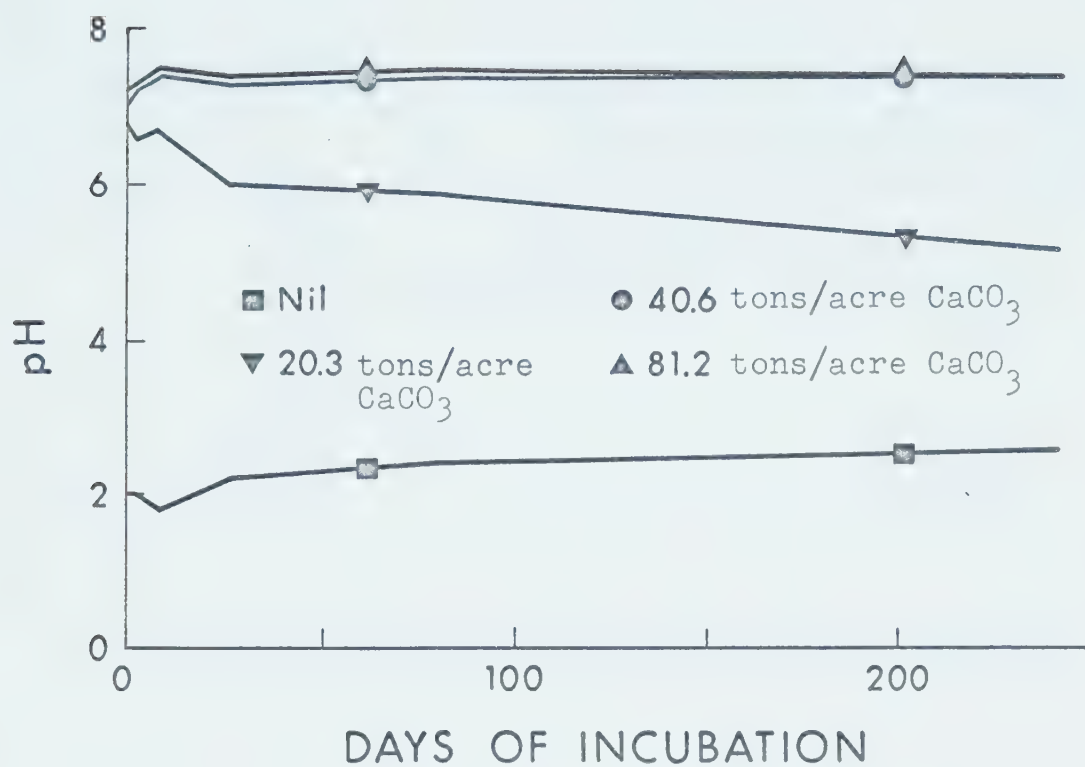


Figure 3: pH and elemental sulfur content of a sulfur-acidified soil (A) after incubation with and without CaCO_3

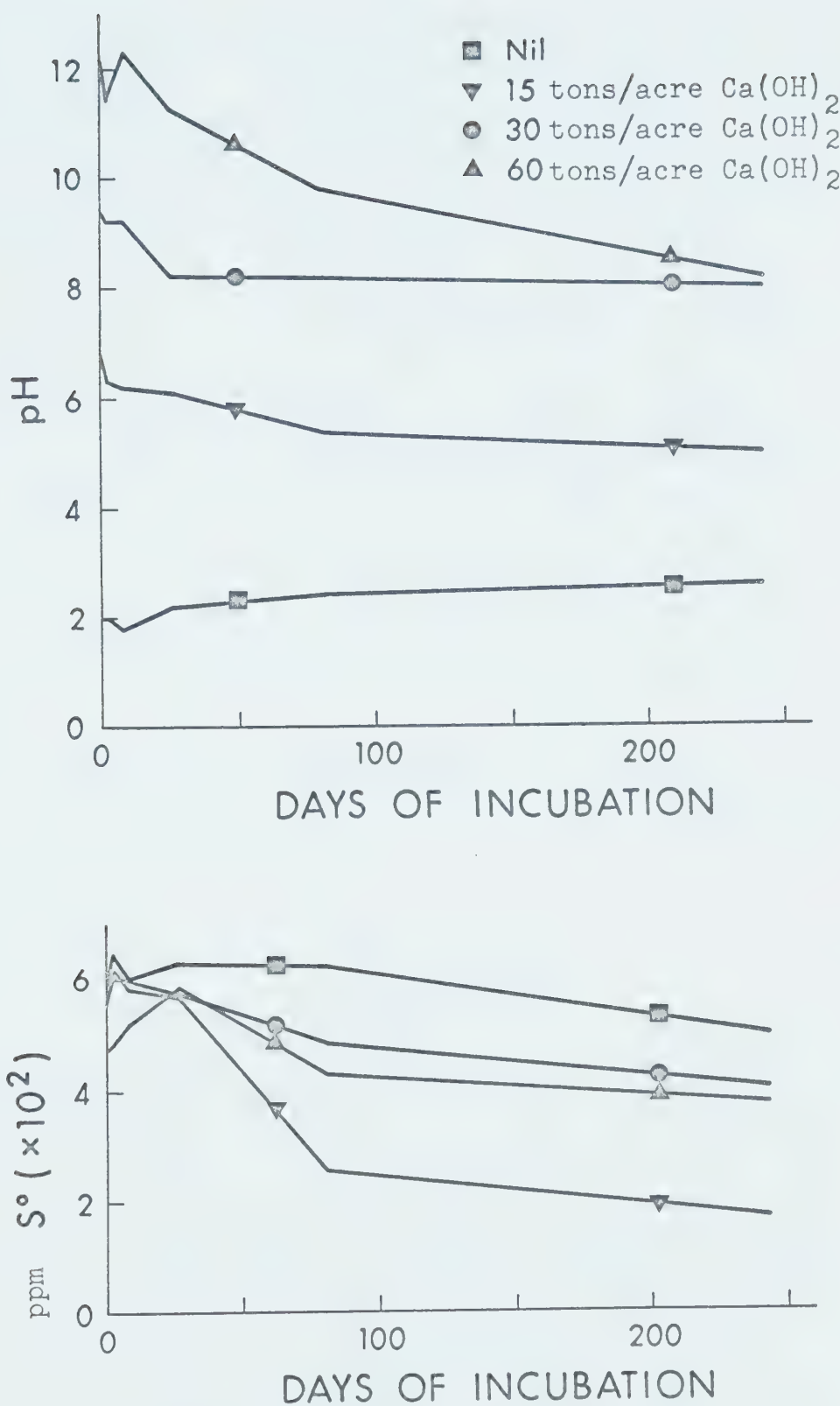


Figure 4: pH and elemental sulfur content of a sulfur-acidified soil (A) after incubation with and without $\text{Ca}(\text{OH})_2$

high Ca(OH)_2 treatments (30 and 60 tons per acre) was gradually lowered to a point where plants could grow. The high rates of CaCO_3 (40.6 and 81.2 tons per acre) did not change in pH due to the buffering action of the CaCO_3 .

The results for soil B were very similar to those of soil A (Table 4 and Appendix II). That is, the low liming rates (5 tons/acre Ca(OH)_2 and 6.5 tons/acre CaCO_3) were eventually lowered below pH 5.0. The high rates of Ca(OH)_2 (10 and 20 tons per acre) raised the pH to values of 8.2 and 9.6, respectively. The high rates of CaCO_3 (13 and 26 tons per acre) maintained the soil pH at neutrality.

The stimulation of H_2SO_4 production, by liming, lowered the pH over time in all but the nil and 26 tons/acre CaCO_3 treatments.

(b) Effect of Lime on Plant Growth:

For the first cropping of soil A, liming had a profound effect on plant growth (Tables 5, 6 and appendix III & IV). There was no plant emergence on soil A when the soil received no lime. But the form of lime also determined the amount of growth on this soil. The plant emergence counted indicated a high rate of germination for all crops on all CaCO_3 treatments (Table 5). The germination rate varied between 60 per cent (for crested wheat grown on the 81.2 tons/acre treatment) and 90 per cent

Table 4. Effect of amount and form of lime on changes in pH of soil B (greenhouse).

Treatment	Soil pH*			
	First Cropping		Second Cropping	
	6 week	12 week	before planting	after harvest
Nil	3.1	3.0	3.1	3.1
5 tons/acre Ca(OH)_2	4.9	4.6	4.6	4.5
10 tons/acre Ca(OH)_2	7.3	7.0	6.8	6.8
20 tons/acre Ca(OH)_2	7.9	7.9	7.6	7.6
6.5 tons/acre CaCO_3	5.0	4.6	4.7	4.6
13 tons/acre CaCO_3	6.9	6.8	6.7	6.9
26 tons/acre CaCO_3	7.2	7.2	7.1	7.2

* Original soil pH 3.6; original elemental sulfur content 600 ppm.

Table 5. Effect of amount and form of lime on average emergence of plants on soil A.

Treatment	Number of plants emerged per pot					
	First Cropping*				Second Cropping**	
	Crested Wheat	Brome	Fescue	Timothy	Oats	Barley
Nil	0.0	0.0	0.0	0.0	0.0	0.0
15 tons/acre Ca(OH) ₂	21	23	24	22	9.0	10
30 tons/acre Ca(OH) ₂	7.3	23	13	11	9.0	9.0
60 tons/acre Ca(OH) ₂	0.0	0.0	0.0	0.0	8.5	8.0
20.3 tons/acre CaCO ₃	24	27	27	26	10	10
40.6 tons/acre CaCO ₃	23	25	26	22	10	10
81.2 tons/acre CaCO ₃	17	26	23	20	9	8.5

* 30 seeds of each grass planted.

** 10 seeds of each cereal planted.

Table 6. Effect of amount and form of lime on average dry weight yield of grasses* and cereals** grown on soil A.

Yields of dry matter (g/pot)				
Treatment	First Cropping*			Second ** Cropping
	1st cutting	2nd cutting	3rd cutting	
Nil	0.0	0.0	0.0	0.0
15 tons/acre Ca(OH)_2	0.53	2.0	2.2	2.2
30 tons/acre Ca(OH)_2	0.06	0.18	0.31	2.4
60 tons/acre Ca(OH)_2	0.0	0.0	0.0	1.8
20.3 tons/acre CaCO_3	0.69	2.0	2.2	2.2
40.6 tons/acre CaCO_3	0.72	1.8	2.3	2.1
81.2 tons/acre CaCO_3	0.68	1.7	2.3	1.8

* Grasses grown were Crested Wheat, Brome, Fescue, Timothy.

** Cereals grown were Oats and Barley.

(for brome and fescue on the 20.3 tons/acre treatment).

The 15 tons/acre $\text{Ca}(\text{OH})_2$ rate promoted plant emergence to the same extent as did the CaCO_3 treatments. But the 30 tons/acre treatment produced significantly less germination and the 60 tons/acre rate prohibited any plants from emerging.

The dry weight yield data, (Table 6) from the first cropping of soil A, indicated results similar to the emergence data. The three CaCO_3 treatments and the 15 tons/acre $\text{Ca}(\text{OH})_2$ liming rate produced plant yield data that were not significantly different. The 30 tons/acre $\text{Ca}(\text{OH})_2$ treatment produced very little plant growth, and the nil and 60 tons/acre treatments produced no growth. Over time, the root systems of the plants became well established resulting in the third cutting yielding much higher than the first.

The emergence and yield results can be attributed to the pH effects of lime application. All CaCO_3 treatments and the 15 tons/acre $\text{Ca}(\text{OH})_2$ treatment raised the soil pH to neutrality. That is, the soil pH region conducive to optimum plant growth was attained by these liming applications. The higher treatments of $\text{Ca}(\text{OH})_2$ raised the pH to a point where plant growth was seriously inhibited.

The treatments of soil B produced similar trends to those of soil A, but the differences were not as marked. This was because the soil was not as harshly acidified and

thus the liming rates were much lower. That is, the soil received treatments of 6.5, 13, and 26 tons per acre of CaCO_3 ; and 5, 10 and 20 tons per acre of Ca(OH)_2 . The emergence results (Table 7) indicate that all treatments (including the nil treatment) promoted plant germination and emergence. The dry weight yield data (Table 8) indicates that the 20 tons/acre treatment of Ca(OH)_2 was the only liming rate to consistently and significantly produce lower plant yields during the first cropping. For some crops (first cutting of brome and fescue) the 10 tons/acre Ca(OH)_2 treatment lowered yields when compared to the CaCO_3 and 5 tons/acre Ca(OH)_2 treatments. Again, the high soil pH values (Table 4) due to overliming with Ca(OH)_2 , caused the growth of plants to be inhibited.

The emergence and yield results from the second cropping of soils A and B were very similar (Tables 5,6,7,8). That is, both oats and barley grew well on all liming treatments. Even the high rates of Ca(OH)_2 produced yields equivalent to those of other treatments. This was apparently due in part to elemental sulfur oxidation. As indicated in figures 3 & 4 considerable elemental sulfur was oxidized after liming of soil A. Elemental sulfur analysis was not done for soil B as the results from the pH determinations indicated elemental sulfur oxidation activity similar to that in soil A. The oxidation of elemental sulfur caused the production of sulfuric acid. The rate of production

Table 7. Effect of amount and form of lime on average emergence of plants on soil B.

Treatment	Number of plants emerged per pot					
	First Cropping				Second Cropping	
	Brome*	Fescue*	Alfalfa*	Oats**	Oats**	Barley**
Nil	12	4.0	0.0	9.0	10	10
5 tons/acre Ca(OH) ₂	27	24	25	9.3	9.7	10
10 tons/acre Ca(OH) ₂	26	21	26	9.7	10	9.3
20 tons/acre Ca(OH) ₂	25	22	20	8.0	9.7	9.3
6.5 tons/acre CaCO ₃	27	24	22	10	10	10
13 tons/acre CaCO ₃	26	26	24	9.7	9.7	9.7
26 tons/acre CaCO ₃	25	27	27	9.3	9.3	9.7

* 30 seeds planted.

** 10 seeds planted.

Table 8. Effect of amount and form of lime on dry weight yield of plants grown on soil B.

Treatment	Yield of Dry Matter (g/pot)							
	First Cropping				Second Cropping			
	Brome	Fescue		Alfalfa*	Oats*	Oats	Barley	
		1st cut	2nd cut					1st cut

Nil	Trace e	0.0b	Trace c	0.0c	0.0d	Trace c	Trace e	
5 tons/acre Ca(OH) ₂	3.6a	2.2a	0.72a	1.5a	2.3a	1.6b	1.9d	
10 tons/acre Ca(OH) ₂	1.9c	2.4a	0.40b	1.1b	2.1ab	1.9ab	2.3b	
20 tons/acre Ca(OH) ₂	0.59d	1.9a	0.21bc	0.91b	1.0c	2.2a	2.5a	
6.5 tons/acre CaCO ₃	3.4a	2.1a	0.88a	1.6a	1.7abc	2.3a	1.9d	
13 tons/acre CaCO ₃	3.3a	2.3a	0.73a	1.5a	1.1bc	2.0ab	2.1c	
26 tons/acre CaCO ₃	2.5b	2.1a	0.67a	1.5a	1.3abc	2.1a	2.2c	

* Only one cut

** Treatment results not followed by the same letter are significantly different at 1% level.

was sufficient in soils A and B to lower soil pH in all Ca(OH)_2 treatments and in the low CaCO_3 treatments. In the low lime treatments, the pH had been decreased to a point where plant growth could be harmed due to reacidification. For example, the barley yields on the 5 tons/acre Ca(OH)_2 and 6.5 tons/acre CaCO_3 treatments of soil B, had been significantly lowered below those of the higher lime applications.

The primary conclusion to be drawn from the greenhouse and incubation experiments involving soils A and B is that CaCO_3 was a much better liming material than was Ca(OH)_2 . If Ca(OH)_2 is to be used to neutralize sulfur-acidified soil, it must only be applied at the rate indicated by the lime requirement. Higher rates of Ca(OH)_2 will only harm plant growth. But the use of the lime requirement rate of Ca(OH)_2 would require a supplemental application at frequent intervals to offset the additional sulfuric acid production due to the stimulation of sulfur oxidation which follows liming.

On the other hand, CaCO_3 applications of rates of up to at least four times the lime requirement did not raise the soil pH above neutrality. Also, excess CaCO_3 will neutralize any increase in acid production.

These results generally agree with Beacher et al. (1952) and Rixon and Sherman (1962) who found that

over-liming a normal acid soil with CaCO_3 did not raise the pH above neutrality while excess $\text{Ca}(\text{OH})_2$ did increase the soil pH to a potentially hazardous level. The previously discussed results, however, were unique with regard to a sulfur-acidified soil.

2. CaCO_3 and MgCO_3 Application to Soils J and K

Since commercial grade limestone may have a small amount of MgCO_3 with the CaCO_3 , an experiment was undertaken to determine the effect of MgCO_3 on the soil and on plant growth. In sulfur-acidified soils the soluble sulfate level is very high. This level may be excessive to the extent of causing the soil to be saline as well as acid. Since MgSO_4 is much more soluble than CaSO_4 , a liming material containing Mg may not alleviate the potential saline condition of the sulfur-acidified soils.

Both soils used for this experiment (J and K) were severely acidified (pH 1.4 to 2.1) bush soils¹ from Waterton. The soils contained a large amount of elemental sulfur (10 to 80 tons/acre).

The soils received a lime application of 10% of the soil weight or 100 tons/acre. The lime form added was various combinations of CaCO_3 and MgCO_3 ranging from 100% CaCO_3 to 100% MgCO_3 .

The main objectives of this experiment were to

¹ Bush soils designates soil located in regions of poplar growth at the Waterton plant site.

determine whether MgCO_3 application would result in plant growth inhibition, and, if so, the level of MgCO_3 at which plant growth was harmed.

(a) Effect of Lime on Plant Growth:

The plant emergence data and dry weight yields of oats showed a marked decline in plant growth as the level of MgCO_3 application increased (Table 9). When more than 5 per cent of the lime applied was MgCO_3 , there was virtually no plant growth.

(b) Effect of Lime on Soil pH and Electrical Conductivity:

The pH results indicate a steady rise with increased levels of MgCO_3 , but the pH value did not rise above 7.4. Thus, soil pH alone would not have caused the drastic reduction in plant growth. The electrical conductivity data, however, indicate that MgCO_3 contributed to the formation of a saline soil. For soil J, the nil and 100 per cent CaCO_3 treatments were considered weakly saline (4 mmhos/cm. to 8mmhos/cm.) and the growth of sensitive crops (e.g. oats) would be slightly inhibited. As MgCO_3 was added to the soil, the soil became moderately saline (8 mmhos/cm. to 12 mmhos/cm.) and all plant growth was inhibited. In soil K, only the 100 per cent CaCO_3 and 95 per cent CaCO_3 -5 per cent MgCO_3 treatments lowered the soil salinity to a weak to moderate salinity level. All other treatments were strongly saline (greater than 12 mmhos/cm.)

Table 9. Effect of amount of $MgCO_3$ on pH and electrical conductivity of soils J and K; and on oat emergence and dry weight yield.

Treatment	Soil J				Soil K			
	pH	E.C. (mmhos/cm)	Emergence* (cm)	Yield(g/pot)	pH	E.C. (mmhos/cm)	Emergence* (cm)	Yield (g/pot)
Nil	2.1	6.9	0.0	0.0	1.4	33	0.0	0.0
100 $CaCO_3$ 0 $MgCO_3$	6.6	7.1	11	0.33	6.6	8.3	10	0.53
95 $CaCO_3$ 5 $MgCO_3$	6.6	8.6	12	0.15	6.7	9.7	12	0.54
75 $CaCO_3$ 25 $MgCO_3$	6.8	10	7.0	trace	6.7	16	9.0	trace
50 $CaCO_3$ 50 $MgCO_3$	6.9	11	7.0	trace	7.0	21	5.3	trace
25 $CaCO_3$ 75 $MgCO_3$	7.0	11	9.0	trace	7.2	23	2.0	trace
5 $CaCO_3$ 95 $MgCO_3$	7.2	11	7.0	trace	7.3	24	0.30	trace
0 $CaCO_3$ 100 $MgCO_3$	7.2	11	2.7	trace	7.4	23	1.0	trace

* 12 seeds of oats planted in each pot.

and plant survival was very limited.

The salinity resulting from MgCO_3 applications was due to the solubility of MgSO_4 versus that of CaSO_4 . As demonstrated by soil K, the sulfate production due to sulfur oxidation was at such high levels that even the nil treatments had a high electrical conductivity. When CaCO_3 was added to the soil, CaSO_4 was formed. This is quite insoluble. Thus sulfate ions were removed from solution and a soil salinity problem did not arise. In the case of MgCO_3 , the resulting MgSO_4 is not as insoluble as CaSO_4 . Therefore, sufficient sulfate remained in solution to cause the development of a saline soil at a neutral pH value.

From this experiment, it can be concluded that a liming material containing more than 5 per cent MgCO_3 will be of dubious value when used to neutralize a sulfur-acidified soil. This conclusion was not found in the literature. Crowther and Walker (1952) even recommend a magnesium liming form if the soil is low in magnesium.

3. Elemental Sulfur Application to Soils A, L, M, Q

The incubation of four soils, after an addition of elemental sulfur, was designed to determine the effect of sulfur on soil pH. Also, the rate of sulfur oxidation and the amount of sulfur oxidized were to be observed.

Soil A was a sulfur-acidified soil with a pH of 2.0. The pH did not decrease over the incubation period. But there was a substantial decrease (3,000 ppm) of elemental sulfur in the sulfur treated soil (figure 5 and appendix V). Soil L was acidified to 3.4 by deposition and subsequent oxidation of elemental sulfur near the Innisfail gas plant. Substantial elemental sulfur was oxidized during the incubation and the pH value decreased to 2.4. Soil M was the same as soil L, but had been limed previously to a pH of 5.5 in the field. Nearly all the sulfur was oxidized after 12 weeks and the pH decreased to 2.5 after 3 weeks. Soil Q was a normal Chernozemic soil with an original pH of 5.9. After 12 weeks, the pH of the treated soil was 2.6 and 8,400 ppm of sulfur had been oxidized.

The results of this study indicated the following:

- i) Sulfur oxidation did not lower the soil pH below 2.0;
- ii) Sulfur oxidation occurred at acid pH values as low as 2.0;
- iii) If a soil was previously acidified and then limed sulfur oxidation and soil reacidification occurred much faster than in a soil that had never been affected by elemental sulfur;
- iv) Approximately 9,000 ppm (9 tons/acre) of elemental sulfur were required to lower the soil pH of a Chernozemic soil (Q) to pH 2.0.

These results agree with Starkey (1925) who found

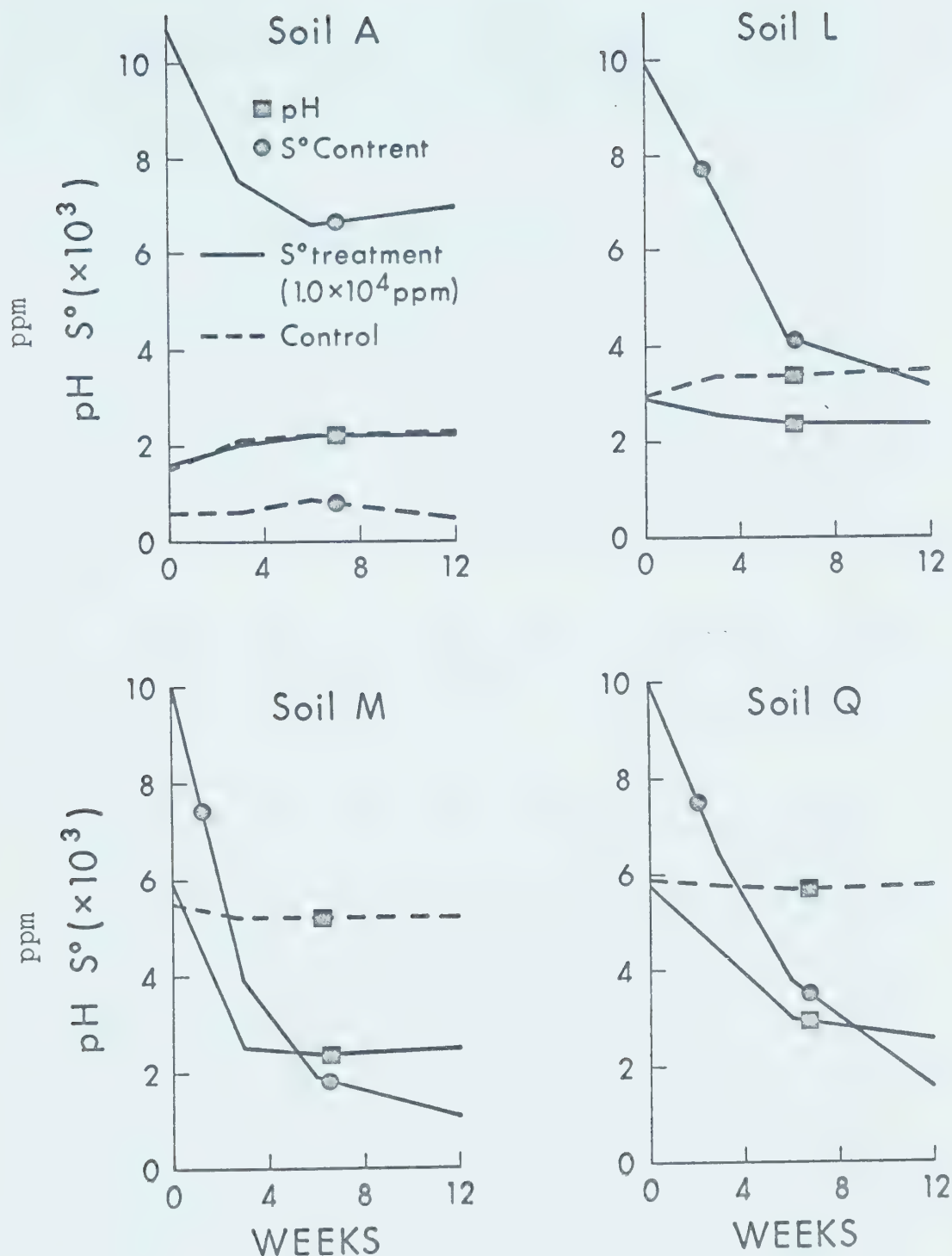


Figure 5: pH and elemental sulfur content of four soils after incubation with and without an application of elemental sulfur.

that T. thiooxidans is active at pH values between 2.0 and 3.0, and that 2.0 is the lower limit of soil pH due to sulfur oxidation.

B. Waterton Field Plot Experiments

The results from the greenhouse and incubation experiments indicated that CaCO_3 could be applied at rates sufficient to compensate for present, as well as potential, soil acidity from sulfur oxidation. The primary purpose of the Waterton field project was to substantiate the laboratory findings. Also, the field experiments were designed to encompass variations in soil structure and texture, soil chemistry, and topography within the acidified area (Plates 1 and 2).

1. Plot 1

The site for plot 1 (Figure 1) was chosen because of the sandiness of the soil, and because the soil was not severely acidified, but contained a significant amount of elemental sulfur. The area surrounding the location supported a sparse growth of brome grass and had a pH of about 3.5. The plot was limed in the fall of 1971 and was then fertilized and seeded in May of 1972. The plot was seeded to brome, alfalfa, oats. But only the oats grew successfully, and was therefore, the only crop harvested. The lack of growth of alfalfa and brome was likely due to the low water holding capacity of the sandy soil. The soil dried sufficiently after planting to hinder efficient germination



Plate 1: General view of some of the area made barren by oxidation of elemental sulfur, and view of elemental sulfur deposition in some of the bush area.



Plate 2: Close-up view of barren soil.

and root growth in the smaller alfalfa and brome seedlings.

The soil pH results indicate a general decrease from May (1972) to October (1972) in the nil, 5 tons/acre Ca(OH)_2 and 6.5 tons/acre CaCO_3 treatments (Table 10). The other higher liming rates (10 tons/acre Ca(OH)_2 , and 13 and 19.5 tons/acre CaCO_3) were sufficient to compensate for any increases in acid production after liming. The high Ca(OH)_2 treatment (10 tons/acre) was not at a rate sufficient to cause the pH to rise above the range conducive to plant growth.

The oat yield results (Table 10) indicate that lime restored the soil's ability to support plant growth. The CaCO_3 treatments yielded the highest level of growth. Although the 6.5 tons/acre treatment had decreased in pH to 4.8, the yield was 50 cwt./acre. The higher CaCO_3 applications yielded 55 and 54 cwt./acre. The 5 tons/acre Ca(OH)_2 had a final pH of 4.2 and a yield of 15 cwt./acre, while the higher rate (10 tons/acre) yielded 42 cwt./acre. Thus, only the 5 tons/acre Ca(OH)_2 treatment yielded poorly. This was due to the lowering of the soil pH by sulfur oxidation stimulation.

2. Plot 3

The plot 3 site (figure 1) was situated on an east-facing slope near an area of dying tree growth. The soil had a loam texture, high elemental sulfur content, and

Table 10. Waterton Plot 1*: effect of amount and form of lime on surface pH and oat yield.

Treatment	pH			Yield (cwt./ac.)
	May 1972	July 1972	Oct. 1972	
Nil	3.6a**	3.0a	3.3a	0.0
5 tons/acre Ca(OH) ₂	5.6b	4.0ab	4.2b	15
10 tons/acre Ca(OH) ₂	6.8b	6.3c	6.8c	42
6.5 tons/acre CaCO ₃	5.6b	4.8bc	4.8b	50
13 tons/acre CaCO ₃	5.6b	5.5bc	6.2c	55
19.5 tons/acre CaCO ₃	6.2b	6.0c	6.6c	54

* Initial pH = 3.5; Initial ppm sulfur = 500 ppm

** Treatment results not followed by the same letter are significantly different at the 5% level.

Table 11. Waterton Plot 3*: surface pH after Ca(OH)₂ additions.

Treatment	pH		
	June 1972	July 1972	Oct. 1972
Nil	2.1	1.9	2.0
10 tons/acre Ca(OH) ₂	4.6	2.6	2.2
20 tons/acre Ca(OH) ₂	6.5	5.3	2.8
10 tons/acre 5.5 tons/acre Ca(OH) ₂	4.8	3.1	2.4

* Initial pH = 2.0; Initial ppm sulfur = 10,000

** 10 tons/acre CaCO₃ applied to 0-6" depth
5.5 tons/acre CaCO₃ applied to 6-12" depth.

was much more seriously acidified than plot 1. The plot was designed to determine whether or not over-liming with $\text{Ca}(\text{OH})_2$ would seriously effect plant growth. Another objective of plot 3 was to determine if liming to a depth of one foot produced more growth than liming the 0-6 inch depth.

Since the plot was located near an area of poplar trees, the air carrying elemental sulfur particles was slowed in this region. Thus, during the winter months of 1971 and 1972, the plot received a large deposition of elemental sulfur (plate 3). As the temperature increased in the spring, the sulfur was rapidly oxidized by sulfur oxidizing bacteria. By early July, the soil pH had fallen from 4.6 to 2.6 on the 10 tons/acre treatment; and by fall the pH had fallen below 3.0 on all treatments (Table 11).

The barley, brome, and reed canary grass planted on plot 3 grew rapidly in June. Plate 4 shows the harmful effects of the soil reacidification during July. The soil acidity killed all plants well before harvest time.

Plot 3 indicates, directly, the effect of not compensating for potential acidity when liming a sulfur acidified soil. The high rates of $\text{Ca}(\text{OH})_2$ did not raise the pH above neutrality. But in order to successfully lime a soil such as plot 3, $\text{Ca}(\text{OH})_2$ would have to be applied repeatedly as more and more acid was produced. $\text{Ca}(\text{OH})_2$ applications that



Plate 3: Sulfur deposition and early plant emergence on plot 3.



Plate 4: Dying plant growth due to elemental sulfur oxidation on plot 3.

would compensate for potential acidity would only result in initial plant harm due to an alkaline pH.

3. Plot 5

The site for plot 5 (figure 1) was on an area of shallow top soil, or mixed top and subsoil. The soil had a poor physical structure and little organic matter. The adverse soil conditions were a result of the clearing of dying trees by heavy equipment. In the process, most of the top soil was removed exposing a dense and stony B horizon. This soil was of a clay loam texture with 0.8% organic matter.

The liming rates for plot 5 were 2, 6, 10, and 24 tons per acre of CaCO_3 . All vegetation (grasses, alfalfa, and oats) grew successfully on the limed plots. Only the oats were sampled for yield measurements as the other plant species were sown by broadcasting making proper sampling difficult.

The 24 tons/acre CaCO_3 treatment was the only rate of lime which prevented the soil pH from decreasing below 6.0 (Table 12). The 6 tons/acre and 10 tons/acre treatments produced a substantial oat yield even though the pH values had fallen to 4.1 and 5.4, respectively. The 2 tons/acre CaCO_3 treatment produced plant growth, but the yield was significantly less than the other treatments. The nil plots also yielded a slight degree of oat growth (Table 12).

Table 12. Waterton Plot 5. effect of amount of CaCO_3 on surface pH and oat yield.

Treatment	pH*		Yield (cwt/ac.)
	July 1972	October 1972	
Nil	3.6a**	3.5a	1.9
2 tons/acre CaCO_3	3.9a	3.6a	9.0
6 tons/acre CaCO_3	4.8ab	4.1a	18.0
10 tons/acre CaCO_3	5.7bc	5.4b	20
24 tons/acre CaCO_3	6.4c	6.3b	21

* Initial pH - 3.5 Initial Elemental Sulfur content

** Treatment results not followed by the same letter are significantly different at 1% level.

4. Plot 6

The location of plot 6 was near a water course which drained the acidified area. The site was selected because of the moist conditions of the soil, the severity of acidification, and the depth of acidification. The soil was severely affected and was comprised mainly of material eroded from cleared areas of the acidified region: The soil was a loam in texture, had 6.0 per cent organic matter, and was acidified to pH 3.5 at a depth of 3 feet.

The pH results (Table 13) indicate that only a liming rate of 29 tons/acre CaCO_3 neutralized the soil and then prevented a fall in pH once sulfur oxidation increased. The 4 tons/acre and 13.5 tons/acre CaCO_3 applications raised the pH to 3.0 and 4.3, respectively (plate 5).

The yield results of the various cereals and grasses grown on plot 6, correspond with the pH values. The greatest yield in all cases was on the 29 tons/acre treatment. The 13.5 tons/acre CaCO_3 treatment resulted in significant growth, but only barley, oats, and reed canary grass grew on the 4 tons/acre treatment. All plants failed to grow when no lime was applied. On all liming treatments, the cereals out-yielded the grasses. For the cereals, oats yielded higher than barley and in the case of grasses the yields were highest for reed canary grass, then timothy, fescue, and brome in that order.

Table 13. Waterton Plot 6: effect of amount of CaCO_3 on surface pH and plant yields

Treatment	pH*		**Yield (Cwt./ac.)					
	July 1972	October 1972	Barley	Oats	Reed Can- ary Grass	Brome	Fescue	Timothy
Nil	2.6c***	2.8 c	0	0	0	0	0	0
4 tons/acre CaCO_3	3.3 c	3.0 c	1.1	7.1	1.2	0	0	0
13.5 tons/acre CaCO_3	4.2 b	4.3 b	23	27	19	7.9	11	15
29 tons/acre CaCO_3	6.1 a	6.2 a	34	37	27	10	13	24

* Initial pH - 3.2 Initial Elemental Sulfur content - 2.7×10^3 ppm

** Yield samples obtained by harvesting two 10 ft. rows from each plot. Some plots had very erratic growth due to acid water washing across plots. Thus some plots could not be sampled randomly.

*** Treatment results not followed by the same letter are significantly different at 1% level.



Plate 5: Limed and unlimed treatments of plot 6.



Plate 6: View of sulfur deposition and barren soil in bush area.

The Waterton plot data verified the greenhouse and incubation results. That is, potential acidity had to be compensated for by excess lime applications. Also, CaCO_3 , when applied at rates exceeding the actual acidity lime requirement, did not raise the pH above neutrality.

The very adequate plant growth indicates that liming plus adequate fertilization was a most effective method of reclaiming extremely acid soils. This coincided favorably with much of the literature concerning cat-clay and coal mine reclamation. Chenery (1954), Hart (1959), and Murakami (1968) indicate that liming greatly improves the chemical status of cat-clays. Hart (1959) also indicates that the lime form must not raise the pH above neutrality. Blevins et al. (1969) recommended liming as the method of reclaiming soil and water acidified by the oxidation of pyrites exposed by strip mining.

Other observations from the plot studies, which were not found in the literature, are that:

- i) Plants grown on the limed soils may be subject to moisture stress during periods of low precipitation, as plant roots survive only in the neutralized soil (this was observed in the greenhouse box experiment discussed under section C).
- ii) Reed canary grass survived well under fairly acid soil conditions.
- iii) Oats consistently grew the best of the various crops

planted.

The field results point out the extreme tolerance of oats to soil acidity. For example, on plot 6, oats yielded 7 times that of barley or reed canary grass on the 4 tons/acre CaCO_3 treatment. The pH of the soil was 3.3 in July and 3.0 in October. Therefore, oats would be the best crop to plant on a limed sulfur-acidified soil in order to quickly restore plant growth to the area.

C. Downward Movement of Lime

The neutralization of acidified subsoil by the downward diffusion of lime was investigated in the field at Waterton during 1972. Also, a laboratory and greenhouse experiment were conducted to further investigate subsoil neutralization. The application of lime below a depth of 6 inches would require large amounts of time, labor, equipment and capital. But, only a 6 inch lime application resulted in an extremely shallow rooting zone where the subsoil was acidified. Hence, the four Waterton field plots were sampled extensively to determine the increase in soil pH, if any, below six inches.

Since the Waterton gas plant (figure 2) is located in an area of strong westerly winds, there is potential for air-suspended particles to be carried for a considerable distance. The tree growth east of the plant site prevented

sulfur from being removed from the Shell, Canada property. The soil in the bush areas was, thus, extremely acidified resulting in serious harm to tree growth. For this reason, three experiments were undertaken to determine whether surface lime application on the bush soil could be expected to, over time, neutralize the acidified subsoil and restore healthy tree growth.

1. Downward Movement of Lime on the Waterton Field Plots:

The results of plot 1 (Table 14) indicate that lime did diffuse downward and increase subsoil pH. For the October, 1972 soil samples, the 10 tons/acre $\text{Ca}(\text{OH})_2$, 13 tons/acre CaCO_3 , and 19.5 tons/acre CaCO_3 liming rates had raised the pH to 6.0 or above to a depth of one foot. The nil treatment had a pH of 4.7 at the one foot depth. The lower liming rates had also significantly raised the soil pH at depth. This rather significant rise in subsoil pH was probably due to the fact that the soil was very sandy and permeable. The results from table 14 indicate that chemically equivalent amounts of $\text{Ca}(\text{OH})_2$ (10 tons/acre) and CaCO_3 (13 tons/acre) were not significantly different as to their ability to neutralize the surface and subsoil, even though $\text{Ca}(\text{OH})_2$ is much more soluble than CaCO_3 .

In plot 3 (Table 15) the soil had been so severely reacidified that there was very little difference between the lime and nil plots. The treatment that was limed to the

Table 14. Waterton Plot 1: effect of form and amount of lime on neutralization of soil acidity below the depth of lime application (0-6").

Treatment	Depth	pH	
		July 1972	October 1972
Nil	0-6	3.0	3.3c*
	6-8	4.3	3.8a
	8-10	4.6	4.4d
	10-12	5.3	4.7d
5 tons/acre Ca(OH) ₂	0-6	4.0	4.2b
	6-8	4.4	4.2a
	8-10	5.0	4.8cd
	10-12	5.4	5.4c
10 tons/acre Ca(OH) ₂	0-6	6.3	6.8a
	6-8	5.6	6.1a
	8-10	6.2	6.0ab
	10-12	6.2	6.1ab
6.5 tons/acre CaCO ₃	0-6	4.8	4.8b
	6-8	5.0	4.8a
	8-10	5.4	5.3bc
	10-12	5.8	5.8bc
13 tons/acre CaCO ₃	0-6	5.5	6.2a
	6-8	5.1	5.5a
	8-10	5.8	5.5abc
	10-12	5.9	6.0abc
19.5 CaCO ₃	0-6	5.9	6.6a
	6-8	4.9	6.0a
	8-10	6.2	6.2a
	10-12	6.1	6.4a

* Treatment results for each depth not followed by the same letter are significantly different at the 5% level.

Table 15. Waterton Plot 3: pH of soil with depth after applications of $\text{Ca}(\text{OH})_2$

Treatment	Depth	pH	
		June 1972	October 1972
Nil	0-6	2.1	2.0
	6-8	2.4	2.2
	8-10	3.0	2.6
	10-12	3.3	3.2
10 tons/acre $\text{Ca}(\text{OH})_2$	0-6	4.6	2.2
	6-8	3.8	2.6
	8-10	3.8	3.1
	10-12	4.0	3.6
20 tons/acre $\text{Ca}(\text{OH})_2$	0-6	6.5	2.8
	6-8	4.4	2.8
	8-10	3.9	3.1
	10-12	3.8	3.3
10 tons/acre* 5.5 tons/acre $\text{Ca}(\text{OH})_2$	0-6	4.8	2.4
	6-8	6.2	3.6
	8-10	6.2	4.1
	10-12	6.2	4.2

* 10 tons/acre applied to 0-6" depth.
5.5 tons/acre applied to 6-12" depth.

one foot depth (10 tons over 5 tons per acre) resisted reacidification at depth to a greater degree than the other treatments. The pH at 12 inches was 4.2 on this treatment versus 3.6 to 3.2 on other lime treatments.

Because of the disturbance of the soil of Plot 5, some sections of the plot were comprised of less affected soils than other parts. That is, unaffected soil was nearer the surface in one section of the plot. Thus, values from the less affected area were discarded when averaging pH determinations for presentation in Table 16. One replicate of each treatment was discarded. The results indicate that the lime had begun to neutralize the soil at the 8 inch depth on the 6, 10, and 24 tons per acre treatments. The high lime treatment had raised the pH at the 12 inch depth.

The plot 6 results (Table 16) were similar to those on plots 1 and 5. That is, the high lime treatment (29 tons/acre CaCO_3) significantly raised the soil pH at the 12 inch depth. The 4 tons/acre CaCO_3 was not significantly better in neutralizing the soil than was the nil treatment. The 13.5 tons/acre treatment significantly lowered the acidity (as compared to the nil treatment) to a depth of 10 inches. The lowering of subsoil acidity by liming was, however, insufficient to neutralize the soil (the 29 tons/acre CaCO_3 treatment had a pH value of 4.3 at the 12 in. depth). Thus,

Table 16. Waterton Plots 5 and 6: effect of amount of CaCO_3 on neutralization of soil acidity below the depth of lime application (0-6")?

Treatment*	Depth	pH**	
		October 1972	October 1972
Nil	0-6	3.5	2.8c**
	6-8	3.6	3.3c
	8-10	3.7	3.5c
	10-12	3.8	3.6b
2 tons/acre CaCO_3	0-6	3.6	3.0c
	6-8	4.0	3.5c
	8-10	3.7	3.6bc
	10-12	3.7	3.8b
6 tons/acre CaCO_3	0-6	4.1	4.3b
	6-8	4.0	3.8b
	8-10	3.9	3.9b
	10-12	3.7	3.9b
10 tons/acre CaCO_3	0-6	5.4	6.2a
	6-8	4.0	4.3a
	8-10	3.7	4.3a
	10-12	3.5	4.3a
24 tons/acre CaCO_3	0-6	6.3	
	6-8	4.8	
	8-10	4.2	
	10-12	4.3	

* Plot 5

** Erratic values

* Plot 6

** Treatment results, for the same depth, not followed by the same letter are significantly different at the 5% level.

the soils remained very acid below the level of lime incorporation.

The Waterton plot results indicate that, over time, the lime had lowered the acidity in soils below the depth of lime application. Nelson (1929) Brown and Munsell (1936) and Longnecker and Sprague (1940) all indicate that lime does move downward over time, but that the process is very slow (10 years for neutralization of the underlying six inches). These findings agree with the results from the Waterton field plots.

2. Downward Movement of Lime on Bush Soils

Since it was desirable to prevent sulfur from leaving the Shell, Canada property as air suspended particles, the bush areas (Plate 6) were hoped to be saved by surface applications of lime. The lime could not be incorporated into the soil, as the necessary heavy equipment would destroy the tree roots. Thus, during 1972 two bush plots (figure 1) were established at Waterton. Both Ca(OH)_2 and CaCO_3 (at rates of 20 tons/acre) were spread on the soil surface and the soils were sampled, subsequently, to determine whether the soil acidity decreased under the limed treatments.

In bush plot 1, the subsoil was not appreciably altered in soil pH by the lime applications (Table 17).

Table 17. Waterton Bush Plots: changes in sub-soil pH after surface applications of CaCO_3 and Ca(OH)_2 .

Treatment	Depth (in.)	pH		
		Bush Plot 1		Bush Plot 2
		August (1972)	October (1972)	Oct. (1972)
Nil	0-1	2.1	1.5	1.8
	1-2	2.4	2.1	2.2
	2-4	2.8	2.5	2.7
20 tons/ acre Ca(OH)_2	0-1	11.9	8.9	9.5
	1-2	3.4	2.9	2.9
	2-4	2.8	3.2	4.2
20 tons/ acre CaCO_3	0-1	5.8	6.0	6.0
	1-2	3.2	2.8	3.1
	2-4	2.9	3.0	4.6

The plot was located near a slough on very moist soil of medium texture. The soil pH was 3.0 to 3.2 on the limed treatments and 2.5 on the nil treatment at a depth of four inches.

On the other hand, bush plot 2 (located on a dry, sandy hill) had a pH of 4.2 to 4.6 on the limed treatments. The nil treatment had a pH of 2.7. As in the case of field plot 1, the downward movement of lime on this plot was probably due to the very sandy and permeable nature of the soil. Also, the CaCO_3 treatment was more effective in neutralizing soil acidity than was Ca(OH)_2 . Thus, as previously stated, the lack of solubility of CaCO_3 did not decrease its effectiveness as a liming material for sulfur-acidified soils.

Soils C and D were used in a greenhouse and laboratory experiment to determine the soil neutralizing ability of a surface application of lime (CaCO_3 in the box experiment and CaCO_3 and Ca(OH)_2 in the tube experiment). Soil C was a surface bush soil containing a very high level of elemental sulfur. Soil D was the bush subsoil located in the field, below soil C. A secondary objective of the experiment was to determine whether removal of the sulfur containing surface soil before liming increased the ability of lime to neutralize the subsoil.

This was to be accomplished by using only soil D

(sub soil) in half of the boxes and tubes, and then lime the top inch. It was thought that by removal of the sulfur-containing surface soil (C), depletion of excess lime by oxidation of elemental sulfur would be prevented. Thus, sub soil acidity may be more readily neutralized than if lime were applied directly to the surface of intact bush soil.

In the greenhouse box experiment CaCO_3 was incorporated into the top inch of soil at a rate of 20 tons/acre. The soils in the boxes were either the intact soil as found in the bush (Soil C over Soil D) or the bush soil with the surface inch of soil removed. After liming the soils were seeded to oats.

The preliminary sampling of the box soils (August, 1972) indicated that the lime had neutralized the inch below the depth of application (Table 18). But the September sampling indicated that the previous results were in error, and the lime had, in fact, not reduced the acidity at all. The August results were in error due to a faulty sampling technique where some of the surface-applied lime was physically mixed with the subsoil. The tube experiment (Appendix VI) also indicated that the lime did not neutralize the acidified subsoil, even though 14 inches of water had been applied over a very short period of time.

The yield and pH results (Table 18) indicated the

Table 18. Effect of a surface application of CaCO_3 on sub-soil pH and oat yield (greenhouse).

Treatment	Soil*	pH		Yield (g/pot)
		Depth	Aug. 8 (1972) Sept. (1972)	
Nil	Intact**	0-1"	1.2	1.3
		1-2"	1.8	1.8
		2-6"	2.4	2.1
	Surface*** Removed	0-1"	2.7	2.6
		1-2"	2.6	2.6
		2-6"	2.5	2.5
20 tons/acre CaCO_3	Intact	0-1"	6.4	2.4
		1-2"	4.4	2.2
		2-6"	2.5	2.4
	Surface Removed	0-1"	7.0	7.0
		1-2"	5.9	2.6
		2-6"	2.7	2.5

* Surface soil: initial pH - 0.9
elemental sulfur content 1.7×10^4 ppm.

Subsoil: initial pH - 2.1
elemental sulfur content 220 ppm.

** Soil is in the condition in which it exists in the field.

*** Sulfur-containing surface inch of soil removed.

speed at which elemental sulfur is oxidized once the soil acidity is lowered. At the beginning of the experiment, the pH of the limed, sulfur-containing, surface soil was 6.4. But after six weeks the pH was lowered to 2.4 and the yield was 0.70 g. of oats. On the other hand, when the sulfur-containing layer was removed before liming the pH remained at 7.0 and the yield was 7.6 g. of oats.

The bush soil experiments indicated very little, if any, neutralization of subsoil acidity after lime application. The only substantial rise in soil pH at depth, after liming, was on bush plot 2, which was on very sandy soil. These findings indicated that surface liming may eventually lower soil acidity to a soil depth helpful to damaged plants. But, for the trees at Waterton, this neutralization would be much too slow to restore health to the poplar stands. The investigation of the soil acidity problem at Waterton brought to light the extreme tolerance of poplar trees to acidity. The trees at Waterton grew after a fashion on soils having pH values as low as 1.5.

Stewart and Wyatt (1919) indicated that, in general, a surface application of lime does not affect the subsoil. This substantiates the results of the bush soil experiments.

D. Chemical Analysis of Acidified, Limed and Unaffected Soils

The purpose of the soil analyses was to determine the effect of acidification, and subsequent liming on soil chemistry. Soils that had not been exposed to sulfur acidification were also analyzed to serve as a comparison to the sulfur-acidified soils.

The soils chosen for chemical analysis were obtained from an incubation, a greenhouse, and a field experiment. The incubation experiment was designed to determine the effect of CaCO_3 and, secondarily, incubation on the chemistry of acidified and normal soils. The lime was applied at a rate sufficient to alleviate present acidity as well as that produced following stimulation of sulfur oxidation as a result of liming. The soils from the greenhouse experiment were soils A and B. These soils had received various rates of $\text{Ca}(\text{OH})_2$ and CaCO_3 and were then used for a total of 24 weeks in the greenhouse. The Waterton plot 6 soils were also analyzed. These soils had received various applications of CaCO_3 in the field.

The chemical analysis of the soils will be discussed, jointly, under the heading of each chemical parameter determined.

1. Ammonium and Nitrate Nitrogen

The major objective of the nitrogen determinations

was to ascertain whether or not acidified soils regained the ability to nitrify ammoniacal nitrogen, after liming. Also, the amount of mineral nitrogen which accumulated after incubation (without lime) was to be determined in order to observe the rate of mineralization of nitrogen under acid and normal soil environments.

The results obtained from the incubated soils indicate that the extremely acidified soils slowly began to regain the ability to nitrify (Table 19). The soils, which had been most severely affected (A, D, B, N, E, and F) accumulated significant nitrate only when limed. But for both the nil and lime treatments, the vast majority of the mineral N remained in the NH_4 form after 6 weeks of incubation. The two less affected acid soils (G and H) accumulated mineral N almost exclusively in the NO_3 form after liming, while the unlimed soils retained the inorganic N as ammonium.

The least acidified soil (O), and the unaffected soils (P and I) accumulated N in the nitrate form for all soils and treatments, despite their rather low pH values (4.6 and 4.8).

The incubated soils contained larger amounts of mineral N than did the corresponding unincubated soil. That is, over a wide range of soil pH values, both limed and unlimed soils accumulated mineral N during incubation.

Table 19. Chemical analysis of soils before and after incubation with and without lime.

Soil	Treatment	pH	ppm Total Mineral	ppm N NH ₄ -N	ppm NO ₃ -N	ppm Avail- able P	ppm SO ₄ -S
A	none	2.1	142	140	2.5	20	5200
	incubation	2.2	262	260	1.6	11	10000
	inc.+ lime	7.0	249	220	29	1.0	1400
D	none	2.4	74	72	2.0	5.5	1600
	incubation	2.5	221	220	0.95	2.5	2000
	inc.+ lime	6.6	258	180	78	2.5	1100
B	none	3.6	56	53	3.5	26	360
	incubation	3.1	162	160	1.9	24	950
	inc.+ lime	6.1	231	180	51	28	950
N	none	3.5	183	140	43	46	1400
	incubation	3.4	268	230	38	43	1700
	inc.+ lime	6.7	314	210	104	11	980
E	none	3.7	35	24	11	13	1400
	incubation	3.6	79	70	8.8	20	1700
	inc.+ lime	7.4	69	60	8.5	13	980
F	none	2.8	234	190	44	3.0	4400
	incubation	2.8	383	380	2.6	1.5	4600
	inc.+ lime	4.6	371	320	51	1.0	2100
G	none	3.5	60	56	4.5	16	280
	incubation	3.2	184	180	4.1	14	850
	inc.+ lime	6.7	244	4.5	240	10	820
H	none	4.6	14	12	2.0	11	260
	incubation	4.4	145	140	5.3	14	440
	inc.+ lime	6.2	224	4.1	220	26	460
O	none	5.1	38	10	28	25	30
	incubation	4.6	173	3.0	170	31	28
	inc.+ lime	6.1	204	3.6	200	18	36
P	none	5.3	42	12	30	32	41
	incubation	4.8	173	3.3	170	24	39
	inc.+ lime	6.0	193	3.0	190	7.5	53
I	none	6.1	17	10	7.0	2.5	19
	incubation	5.5	214	4.4	210	2.5	19
	inc.+ lime	6.3	204	4.2	200	2.0	19

m./100 g. extractable				ppm extractable	
K	Ca	Mg	Na	Al	Mn
0.38	2.0	4.3	0.10	1000	19
0.38	2.6	4.9	0.12	1400	22
0.54	34	3.7	0.11	1.3	2.0
0.34	3.0	2.3	0.08	780	54
0.61	3.9	2.7	0.08	1100	92
0.52	34	2.0	0.08	2.8	3.0
0.16	4.0	0.83	0.06	310	46
0.33	4.8	0.82	0.06	580	120
0.28	18	0.82	0.06	4.5	3.8
0.66	10	1.5	0.07	570	150
0.79	19	2.0	0.08	750	280
0.73	33	1.6	0.08	1.0	9.0
0.28	13	3.8	0.07	590	90
0.40	16	4.7	0.08	600	140
0.35	30	1.6	0.06	1.0	3.0
0.44	9	2.1	0.20	1500	80
0.61	14	2.4	0.20	1400	88
0.42	37	2.4	0.19	46	47
0.38	1.5	0.62	0.04	670	44
0.46	2.3	0.82	0.06	930	120
0.34	23	0.41	0.04	2.5	2.0
1.8	16	2.5	0.06	64	26
2.1	15	2.4	0.06	32	72
1.8	22	1.8	0.06	1.0	trace
1.0	16	1.9	0.06	4.0	32
1.1	18	2.0	0.06	4.5	30
1.0	20	1.6	0.06	0.50	trace
1.4	16	1.9	0.06	2.5	38
1.5	16	1.8	0.06	3.2	22
1.4	20	1.6	0.06	0.75	trace
1.1	17	4.0	0.05	1.5	2.5
1.2	19	4.1	0.06	1.0	trace
1.1	18	2.7	0.05	0.75	trace

Alexander (1961) states that organic N accumulates in acid soils so that a rapid release of mineral N is noted when such soils are limed. This phenomenon was not noted in the incubated soils as some soils (e.g. A) accumulated more mineral N when incubated without lime. Since severely acid soils contain less viable ammonifiers than do neutral soils (Alexander 1961), the large mineralization of N in the acid soils can be explained by assuming that the process was both biological and chemical. That is, the product of organic N mineralization by microbes and incubation with sulfuric acid is ammonium.

The analysis of the greenhouse soils (A and B) indicated that acidified soils fully regained the ability to nitrify after liming (Table 20). For all liming rates on both soils, any mineral N accumulation was largely in the nitrate form. On the other hand, the nil treatments accumulated nitrogen as ammonium. The two low liming rates on Soil A (15 tons/acre Ca(OH)_2 and 20.3 tons/acre CaCO_3) and the 6.5 tons/acre CaCO_3 treatment on Soil B showed a slightly higher NH_4 level than did the other liming treatments. This indicated an effect of under liming sulfur acidified soils. The stimulation of sulfur oxidation by liming, had caused more acid to be produced and thus the soil pH values were lowered. The pH of these soils had been lowered sufficiently to, again, inhibit the nitrifying organisms. Soils A and B were used in a greenhouse experiment, and thus received N in the form of fertilizer. Also,

Table 20. Chemical analyses of soils A and B before and after applications of different amounts of Ca(OH)_2 and CaCO_3 .

Soil Letter	Treatment	pH	ppm $\text{NH}_4\text{-N}$	ppm $\text{NO}_3\text{-N}$	ppm avail. P	me/100g. K	ppm $\text{SO}_4\text{-S}$
A	original soil	2.1	140	2.5	20	0.38	5200
	nil	2.4	300	80	13	0.36	8400
	15 tons/acre Ca(OH)_2	5.0	16	20	6.8	0.01	1400
	30 tons/acre Ca(OH)_2	7.8	8.4	190	1.5	0.04	1100
	60 tons/acre Ca(OH)_2	9.4	7.0	97	0.5	0.02	1000
	20.3 tons/acre CaCO_3	5.2	9.2	31	6.2	0.01	1400
	40.6 tons/acre CaCO_3	7.2	5.5	51	1.5	0.02	1200
	81.2 tons/acre CaCO_3	7.2	5.6	43	1.0	0.02	1200
B	original soil	3.6	53	3.7	26	0.16	360
	nil	3.1	250	100	46	0.36	820
	5 tons/acre Ca(OH)_2	4.6	0	1.1	46	0.01	920
	10 tons/acre Ca(OH)_2	6.8	3.4	2.9	34	0.04	850
	20 tons/acre Ca(OH)_2	7.6	4.2	87	11	0.02	600
	6.5 tons/acre CaCO_3	4.7	14	2.4	44	0.01	950
	13 tons/acre CaCO_3	6.7	3.6	28	36	0.02	1400
	26 tons/acre CaCO_3	7.1	2.9	38	26	0.02	850

Ca	me/100g.	Na	ppm	Mn
	extractable Mg		extractable Al	
2.0	4.3	0.10	1000	19
1.8	3.8	0.16	1400	23
1.6	1.6	0.13	17	9.2
18	1.0	0.13	1.8	0.5
11	0.41	0.13	2.0	0.5
8.5	0.82	0.12	7.0	6.2
22	1.3	0.06	1.2	1.0
12	0.82	0.06	1.0	0.75
<hr/>				
2.1	0.40	0.06	310	46
2.5	0.41	0.14	540	140
6.6	0.41	0.12	19	45
16	0.62	0.12	3.0	1.5
16	0.62	0.12	8.3	1.0
5.5	0.41	0.12	15	4.5
18	0.41	0.12	4.5	1.0
13	0.41	0.13	4.0	1.0

the plants grown on these soils had removed considerable amounts of N. Therefore, no comparison can be made between treatments as to the effect of lime form and amount on soil mineralization.

The nitrogen analysis of Waterton plot 6 verified the greenhouse results, (Table 21). That is, when lime was applied at rates sufficient to neutralize soil acidity, the acidified soils eventually regained a viable population of Nitrosomonas and Nitrobacter.

The nitrogen results generally agree with Jackson (1967) and Kamparth and Foy (1971). They state that ammonium will accumulate at low soil pH values. This is because the soil contains acid tolerant ammonifying organisms, but no acid tolerant nitrifiers.

2. "Available" Phosphorus (Miller and Axley, 1956)

In the incubated soils (Table 19), phosphate was generally made less "available" by liming. Although low soil pH renders soil phosphate unavailable (Jackson 1969), liming, apparently only enhanced this problem. The unaffected soils (P and I) also indicated a marked reduction in "available" phosphate levels after the soils were incubated with CaCO_3 .

The "available" phosphate recovered from the greenhouse soils (A and B), was much lower on the high lime treatments as compared with the nil or low liming rates (Table 20). For example, on soil B the "available" phosphate level in the 5 tons/acre $\text{Ca}(\text{OH})_2$ and 6.5 tons/acre CaCO_3 treatments was as high as the nil treatments. Even though equal amounts

Table 21. Chemical analyses of Plot 6 after application of various amounts of CaCO_3 .

Treatment	pH	ppm ⁺ NH_4 -N	ppm ⁻ NO_3 -N	ppm avail. P.	me./100g. extract.K ⁺	ppm SO_4 -S
Nil	2.8	230	18	8.8	0.39	5500
4 tons/acre CaCO_3	3.0	200	20	2.2	0.32	2800
13.5 tons/acre CaCO_3	4.3	130	36	1.1	0.22	1700
29 tons/acre CaCO_3	6.2	73	110	1.4	0.26	1200

Treatment	pH	me./100g extract.Ca	me./100g extract.Mg	me./100g extract. Na	ppm extract.	Al	ppm extract. Mn
Nil	2.8	12	2.2	0.14	820		51
4 tons/acre CaCO_3	3.0	22	2.2	0.18	690		46
13.5 tons/acre CaCO_3	4.3	35	2.4	0.14	230		26
29 tons/acre CaCO_3	6.2	38	2.0	0.13	1.4		8.8

of fertilizer P were added to all treatments, the low liming rates retained significantly more of this phosphate in an "available" form. The greenhouse soil results may point out a problem caused by excess lime applied for the purpose of neutralizing potential acidity. The excess Ca reacted with soluble phosphates forming a relatively insoluble compound. However, this apparent lowering of "available" P in the higher liming treatments was not accompanied by a corresponding decrease in plant uptake of P (as observed in the plant analysis studies discussed in section E). Since the Miller and Axley (1956) method was designed to extract plant available P from slightly acid, low Ca soils, this method may not remove as much P as is actually available to plants from soils with a high pH value and/or high Ca content.

The results of plot 6 soil analysis (Table 21) indicated, also, that lime decreased the "availability" of soil phosphate.

Tomlinson (1957) suggested that liming reverses the effects of acidity in cat-clay soils. That is, liming increases phosphate availability. But, all phosphate results obtained from the incubation, greenhouse, and field soils, disagree with this observation. Hart (1959) states that cat-clays require heavy phosphate applications in conjunction with liming in order to fully reclaim the soils.

3. Sulfate-sulfur

Due to the very large amounts of elemental sulfur

deposited on some of the soils (as high as 20 tons/acre), the oxidation of elemental sulfur may cause the production of sulfate to be at a rate sufficient to cause some soils to be saline as well as acidic. In the second greenhouse experiment, the electrical conductivity results (Table 9) indicated that soil K was actually a saline soil as well as being very acidic. Thus, sulfate-sulfur was determined on the incubation, greenhouse, and field plot soils to observe the effect of lime on the soluble sulfate levels of sulfur-acidified soils.

The incubated soils (Table 19) showed that the sulfur-acidified soils had an extremely high level of soluble $\text{SO}_4\text{-S}$ (as high as 1.0% in soil A) as compared to the unaffected soils P and I. But the CaCO_3 application significantly lowered the soluble sulfate level in soils containing more than 1,000 ppm $\text{SO}_4\text{-S}$ when not limed. This lowering of the amount of soluble sulfate by lime was probably due to the formation of CaSO_4 which has a solubility of 2,000 ppm in cold water. The acidified soils exceeded this solubility limit, if all the sulfate in the soil reacted only with Ca. For example, soil B had approximately 2,400 ppm sulfate in the soil solution. Therefore, a substantial amount of the sulfate reacted with other cations, such as K, Mg, and Na, to form compounds which are more soluble than CaSO_4 .

The application of lime did, however, reduce the threat of creating a saline soil situation as the result of

elemental sulfur oxidation. In the case of soil A, the sulfate-sulfur level after incubation was 10,000 ppm, but after incubation with lime the level was 1,400 ppm. According to Richards (1969) the electrical conductivity of a 6,200 ppm SO_4 solution (Na_2SO_4) would be 12 mmhos/cm. The conductivity of a 620 ppm sulfate (Na_2SO_4) solution would be 1.6 mmhos/cm. Thus, the results from the incubation experiment indicate that the addition of CaCO_3 prevented the development of soil A into a saline soil.

In the acidified soils, there was a general rise in the sulfate level during incubation without CaCO_3 (e.g. soil N, before incubation had 1,400 ppm $\text{SO}_4\text{-S}$, while it contained 1,700 ppm after). This was due to sulfur oxidation during incubation. In the second incubation experiment (figure 5 and appendix V), soil A oxidized 3,000 ppm of elemental sulfur over a 12 week period even though the soil had a pH value of 2.0.

The greenhouse soil A (Table 20) also exhibited a marked decrease in $\text{SO}_4\text{-S}$ in the lime treatments. But excess lime did not reduce the soluble sulfate level below that of the low liming applications, to any great degree. A 20 tons/acre application of CaCO_3 lowered the soluble sulfate level from 8,400 ppm to 1,400 ppm. A 81.2 tons/acre addition of lime only reduced the sulfate to 1,200 ppm.

For soil B (Table 20) lime had no reductive effect,

compared to the nil treatment, as to the $\text{SO}_4\text{-S}$ content of the soil. This was because of the relatively low sulfate content of soil B (820 ppm $\text{SO}_4\text{-S}$ on the unlimed treatment).

The results for Waterton plot 6 (Table 21) indicate that the rate of lime that raised the soil pH to neutrality was also the rate which decreased the soluble sulfate level the most. There were 2,800 ppm $\text{SO}_4\text{-S}$ in the 4 tons/acre CaCO_3 treatment and 1,200 ppm in the 29 tons/acre treatment.

4. Extractable¹ Potassium, Calcium, Magnesium, and Sodium

K, Ca, and Mg exhibited the same trend when comparing the pre-incubated soils to the unlimed incubated soils (Table 19). That is, in the case of the acid soils (A, D, B, N, E, F, and G) there was a general increase in extractable K, Ca, and Mg after incubation (without lime). This can be explained by observing the increase in Al upon incubation. The soluble Al ions displaced divalent and monovalent cations (e.g. K, Ca, and Mg) from the cation exchange complex and, thus made these cations more easily extractable.

For example, soil D showed an increase from 780 ppm to 1,100 ppm of extractable Al after incubation. This increase was accompanied by an increase of 0.34 me./100 g. to 3.9 me./100 g. for Ca; and 2.3 me./100 g. to 2.7 me./100 g. for Mg.

¹ Extractable denotes easily soluble plus exchangeable ions.

Certain elements in some soils did not exhibit this trend (e.g. me./100 g. Mg in soil B). This was probably due to a low total Mg level in this soil. That is, nearly all of the Mg in soil B could be removed by the extracting solution regardless of the increase in the Al level.

The less affected and normal soils (H, O, P, and I) had nearly the same K, Ca, and Mg levels before and after incubation. Also, the Al levels did not increase during incubation.

Sodium was not affected by incubation. This was due to the very low levels of Na in the soils, plus the fact that Na is easily displaced from the exchange complex. Therefore, all exchangeable Na was easily extracted and increases in complementary soil cations did not result in an increase in soil solution levels of Na.

Incubation of the soils with lime, generally decreased the amount of K and Mg which could be extracted when compared to the soils incubated without lime. Ca levels were, of course, drastically increased by the addition of CaCO_3 to the soils. This lowering of K and Mg levels was probably due to the drastic decrease in extractable Al after liming. Since Al is much more effective in displacing other cations from the exchange complex, than is Ca, more K and Mg would have been available to the soil solution before liming.

Again, extractable Na levels were unchanged by either soil acidity or liming.

The incubation results for K and Mg disagree somewhat with the findings of Kamparth and Foy (1971). They stated that naturally acid soils decreased K and Mg availability to plants. From the results presented in Table 19 this conclusion cannot be drawn. That is, increasing soil acidity has tended to increase extractable K and Mg, and liming did not raise extractable K and Mg levels over those found in the acidified soils.

The greenhouse soils (A and B) were cropped twice. The first cropping was for 18 weeks and the second was for 6 weeks. Since numerous plants (for a total of 24 weeks) were grown on the soils, it was difficult to draw conclusions as to the effect of acidity and subsequent liming on nutrient levels in the soils. That is, comparisons between nil and limed treatments could not be made as there was considerable plant growth on the limed treatments. Also, in the case of K, it was applied before each experiment in the form of fertilizer. But, general statements can be made concerning K, Ca, Mg, and Na levels in these soils.

Extractable K was very low on all limed treatments on both soils. Although the nil treatment contained 0.36 me./100 g. of K for both soils A and B, the limed treatments had as low as 0.01 me./100 g. (Table 20). This would indicate a

substantial removal of K by the plants. Thus, in reclamation of sulfur acidified soils, an application of K as a fertilizer would be recommended.

In soil A, the Mg level was lowered in all lime treatments as compared to the nil treatment. Also, the high liming rates (60 tons/acre Ca(OH)_2 and 81.2 tons/acre CaCO_3) further reduced the extractable Mg level over that of the lower liming rates. Again, very high amounts of lime may cause nutrient deficiencies of elements such as Mg.

The Mg level remained unchanged by liming in soil B. This was likely a result of the lime applications being insufficient to alter the exchangeable status of Mg.

The Ca levels were much greater in all the limed treatments for both soils because of the large amounts of lime applied to soil A and B.

In both soils A and B, the extractable Na level seemed to be unaffected by liming, except for the very high CaCO_3 rates (40.6 and 81.2 tons per acre) on soil B. These treatments of CaCO_3 had reduced the amount of extractable Na from 0.16 me/100 g. on the nil treatment to 0.06 me/100 g. on the CaCO_3 treatments.

On Waterton plot 6 (Table 21), the K levels had been lowered on the lime treatments as compared to the nil treatment. But, as in the case of the greenhouse soils A

and B, there was plant growth on the treatments receiving CaCO_3 . Thus, it was difficult to conclude whether all the K was removed by plant growth, or whether some of the decrease was due to the lowering of K extractability by liming.

The levels of Mg on plot 6 seem to have been unaffected by liming. But industrial CaCO_3 was used to lime plot 6 (and all Waterton field plots). This liming form contained up to 5 per cent MgCO_3 . Therefore, substantial Mg was added when liming the soil. Hence, no conclusions can be drawn from plot 6 as to the effect of CaCO_3 on the extractable levels of Mg in the soils.

As in the incubation and greenhouse soils, liming did not alter the extractability of Na in plot 6.

The determination of K, Ca, Mg, and Na levels before and after incubation with and without lime, before and after application of various rates of Ca(OH)_2 and CaCO_3 to soils in the greenhouse; and after applying CaCO_3 to a field soil indicated the following:

- i) Incubation of acid soils without lime increased the K, Ca, Mg levels extractable from the soils.
- ii) Liming did not increase the extractable K and Mg in the acidified soils, and there were indications that the extractable levels of K and Mg were decreased by lime.
- iii) Na levels in acidified, limed, and unaffected soils

were not affected by soil acidity or liming.

- iv) When liming sulfur-acidified soils, K should be applied as a fertilizer.
- v) Liming dramatically increased the Ca level in the soils. Thus, the natural ratio of Ca to other elements, such as Mg, was altered considerably.

5. Extractable Al and Mn

In the incubation soils, the Al and Mn levels rose markedly after incubation without lime on the acidified soils (A, D, B, N, E, F, and G). As the hydrogen ion activity of a soil increases, the solubility of Al compounds also rises. As seen in the first incubation experiment (figure 3), considerable elemental sulfur was oxidized by acidified soils during incubation. This increased the soil activity of hydrogen, resulting in increased levels of Al in solution. The same reasoning holds for Mn. For example, soil D, before incubation had 780 ppm Al and 54 ppm Mn. After incubation, the soil contained 1,100 ppm Al and 92 ppm Mn in an extractable form.

Incubation of the acidified soils with CaCO_3 , severely reduced the solubility and, thus, extractability of both Al and Mn. For example, soil D had a level of 2.8 ppm Al and 3.0 ppm Mn after liming (Table 19).

Blevins et al. (1969) stated that Al is the primary

cause of acid soil infertility in a sulfur-acidified soil as a result of strip mining in Kentucky. He further stated that lime readily neutralizes the aluminum toxicity. The results presented in Table 19 support these findings totally.

The greenhouse soils (A and B) which contained up to 1,400 ppm Al (in soil A) and 140 ppm Mn (in soil B) indicate very little extractable Al and Mn on all liming treatments. The low liming rates of soil A (15 tons/acre Ca(OH)_2 and 20.3 tons/acre CaCO_3) and soil B (5 tons/acre Ca(OH)_2 and 6.5 tons/acre CaCO_3), however, showed an increase in Al and Mn levels over the higher liming rates (Table 20). These low lime treatments also had a pH near 5.0 or lower. The higher Al and Mn contents and low pH was a result of sulfur oxidation stimulation by lime. The liming rates were not sufficient to compensate for potential acidity due to elemental sulfur oxidation.

The plant yield results from plot 6 (Table 13) indicate that only the high liming rate (29 tons/acre CaCO_3) produced adequate plant growth. When observing the chemical analysis of plot 6 soil (Table 21) the reason becomes evident. The Al level of the nil treatment was 820 ppm, while the lower lime treatments contained 690 ppm Al and 230 ppm Al. The 29 tons/acre application had, however, reduced the Al level to a non-toxic amount of 1.4 ppm.

SUMMARY

The analysis of these acidified, limed, and unaffected soils has yielded some insight into the effect of severe acidity and heavy liming of some soils. The primary observations afforded by the soil analysis results were:

- i) The soil nitrifying bacteria eventually regained the ability to nitrify after extremely acidified soils were limed sufficiently.
- ii) Considerable organic nitrogen was mineralized even at soil pH values of 2.0.
- iii) Liming reduced the amount of "available" phosphorus in a soil.
- iv) The large amounts of lime required to neutralize some sulfur acidified soils, severely distorted the Ca:Mg ratio of the soils.
- v) The soluble $\text{SO}_4\text{-S}$ content of a soil was reduced to below 1,500 ppm by lime applications sufficient to neutralize the soil acidity.
- vi) The extractable Al and Mn levels were drastically increased by sulfur acidification of a soil. The very high Al content was definitely the major cause of the sterility of these soils.
- vii) Liming reduced the solubility of Al to levels which did not inhibit plant growth.

E. Chemical Composition of Plants Grown on Acidified, Limed, and Unaffected Soils

From the chemical determinations on the limed and unlimed soils (section D) various chemical parameters of the soils were observed to have been considerably altered by sulfur acidification and subsequent liming. These alterations included very high Al, Mn, and SO_4 levels in the acid soils; an increased Ca:Mg ratio and a lowered phosphate availability (as measured by the Miller and Axley, 1956, soil extraction method) in the limed soils. Hence, the chemical composition of plants grown on acidified and limed soils was determined on samples of whole oat plants, oat grain, and whole barley plants. The purpose of plant analyses was to observe the effect of soil acidity and liming on the chemical composition of the plants grown on these soils.

1. Chemical Analysis of Whole Oat Plants:

The whole oat plants from the second cropping of greenhouse soils A and B, and from Waterton plots 1 and 6 were used for chemical analysis. These plants were chosen for analysis in order to compare the effect of various rates of lime on the chemical composition of oats grown on sulfur-acidified soils.

(a) N and S content of whole oat plants:

The oats grown in the greenhouse were harvested six weeks after planting; while the oats from the Waterton

field plots were harvested before full maturity at approximately the soft dough stage of development.

Chapman (1966) stated that 18 day old oat plants normally contain an average of 5.9 % N. Oat straw at harvest has a range of 1.0% to 1.1% N. Oat hay ranges from 1.1% to 1.9% N (U.S. - Canada Feed Tables, 1969).

For oat sulfur levels, the U.S. - Canada Feed Tables (1969) give the intermediate range for oat straw as 0.21% S to 0.27% S. Oat straw is deficient in S if the percentage is less than 0.06 (Chapman 1966).

The greenhouse oat plants could be considered between oat hay and young (18 day) oats as to the stage of development when harvested. Thus, the N content of these plants should range from 2.0% to 6.0% N, with the majority being closer to the 2.0% level of N. The results presented in Table 22 indicate that all of the oats from the greenhouse experiment (except those from the 5 and 10 tons/acre $\text{Ca}(\text{OH})_2$ treatments contained greater than 4.0% N. This relatively high level of N was probably due to the very adequate fertilization of soils A and B. Each soil received a total of 400 ppm N during the course of two greenhouse croppings.

The total S content of the greenhouse oat plants exceeded the intermediate range (0.21% to 0.27%) in all cases (Table 22). This was a consequence of the extremely

Table 22. Elemental analysis of whole oat plants grown on soils (A and B) that had received applications of different amounts of Ca(OH)_2 and CaCO_3 .

Soil	Treatment	pH	% N	% P	% K	% S
A						
	15 tons/acre Ca(OH)_2	4.6	4.3	0.28	2.0	1.0
	30 tons/acre Ca(OH)_2	7.5	5.0	0.30	4.0	0.70
	60 tons/acre Ca(OH)_2	8.1	5.3	0.23	5.4	0.40
	20.3 tons/acre CaCO_3	5.0	4.3	0.23	1.8	0.54
	40.6 tons/acre CaCO_3	7.2	4.9	0.30	2.1	0.42
	81.2 tons/acre CaCO_3	7.3	5.1	0.35	2.9	0.38
B						
	5 tons/acre Ca(OH)_2	4.5	2.6	0.40	3.4	0.64
	10 tons/acre Ca(OH)_2	6.8	3.6	0.36	3.5	0.39
	20 tons/acre Ca(OH)_2	7.6	6.0	0.32	3.4	0.42
	6.5 tons/acre CaCO_3	4.6	5.0	0.36	2.3	0.35
	13 tons/acre CaCO_3	6.9	5.6	0.31	2.6	0.41
	26 tons/acre CaCO_3	7.2	5.0	0.31	2.9	0.38

% Ca	% Mg	% Na	ppm Al	ppm Mn	ppm Zn	ppm Fe
0.60	0.72	0.22	38	180	162	140
1.2	0.42	0.08	18	50	188	140
1.2	0.25	0.06	12	50	188	140
0.90	0.83	0.29	18	200	250	125
1.1	0.71	0.25	12	38	180	170
1.0	0.72	0.37	18	50	168	140
1.2	0.32	0.02	25	580	150	170
1.3	0.32	0.04	38	110	260	175
1.8	0.42	0.06	32	150	250	175
1.1	0.40	0.13	25	590	275	175
1.6	0.32	0.22	32	150	168	170
1.7	0.30	0.13	25	150	188	138

high soluble sulfate levels observed to be present in sulfur-acidified soils; whether limed or unlimed (Table 19).

The oats grown on Waterton plots 1 and 6 contained a normal level of N, but the S content was, again, well above normal (Table 23). The lower N levels of these oat plants, as compared to the greenhouse oats, could have been due to lower N levels in the plot soils.

Tisdale and Nelson (1966) indicated that the N:S ratio for whole oat plants, when grown on soils containing very adequate levels of S, should be, on the average, 6.0 to 1.0. They further stated that a range of 10:1 to 20:1 is suitable for the N:S ratio of plant material to be fed to ruminants. For the oats grown on soil A, the N:S ratios ranged from 4.3:1 (on the 15 tons/acre Ca(OH)_2 treatment) to 13.5:1 (on the 60 tons/acre Ca(OH)_2 and 81.2 tons/acre CaCO_3 treatments). On soil B, the oat N:S ratios ranged from 4.0:1 (on the 5 tons/acre Ca(OH)_2 treatment) to 14:1 (on the 20 tons/acre Ca(OH)_2 treatment). These values indicate a very low N:S ratio on the low lime treatments. The N:S ratio, then, increased with an increase in the rate of liming. The results from Table 22 indicated that the higher liming rates did not appreciably lower the soil soluble sulfate level over that of the low lime treatments. But the oat N:S ratios point out that liming may have

resulted in the decreased uptake of SO_4 in the plants grown on the high lime treatments (Table 22).

The oats from the Waterton field plots (Table 23) all had an N:S ratio of approximately 5:1. Thus, the liming rates were not sufficient to interfere with uptake of SO_4 by the oat plants.

When compared to the N:S ratios presented by Tisdale and Nelson (1966), the N:S ratios of the greenhouse and field oat plants were not abnormal.

(b) P Content of Whole Oat Plants:

Chapman (1966) gives a range for mature oat plants from low (0.16% P) to high (0.40% P).

The oats grown on the greenhouse soils (A and B) fell within the above P content range, even though the chemically extractable ("available") P levels in the soil were very low on the high lime treatments (Table 20). The large Ca applications lowered the "available" P in the soil, but did not inhibit the uptake of adequate P by the plant roots. These results showed an inadequacy of chemical extraction technique which attempted to remove from the soil the amount of P available to the plant. The analysis of the oat plants indicated that the amount of soil P actually in a plant available form was much higher than indicated by chemical analysis of the soil.

Table 23. Elemental analysis of whole oat plants grown on Waterton Plots 1 and 6 after soils had received two rates of CaCO_3 .

Plot	Treatment	pH (Soil)	% N	% P	% K	% S
1	6.5 tons/acre CaCO_3	4.8	1.9	0.15	2.6	0.40
	13 tons/acre CaCO_3	6.2	1.8	0.15	2.5	0.34
6	4 tons/acre CaCO_3	3.0	2.4	0.09	1.7	0.40
	29 tons/acre CaCO_3	6.2	2.8	0.15	2.4	0.52

Plot	Treatment	pH (Soil)	% Ca	% Mg	% Na	ppm Al	ppm Mn	ppm Fe	ppm Zn
1	6.5 tons/acre CaCO_3	4.8	3.3	1.2	0.005	36	100	72	32
	13 tons/acre CaCO_3	6.2	3.8	1.3	0.006	34	100	74	28
6	4 tons/acre CaCO_3	3.0	1.8	1.6	0.13	490	200	200	48
	29 tons/acre CaCO_3	6.2	4.4	2.2	0.23	220	210	190	46

The oats from the Waterton plots (Table 23) had a low P content (0.09% to 0.15%), and the oats from the low lime treatment on plot 6 may have even been deficient in P (0.09%). In this case, the estimation of plant available P by chemical means was correct. Both the soil (Table 21) and plant P levels were low for plot 6. The deficient level of P in the oats grown on the 4 tons/acre CaCO_3 treatment of plot 6, was likely due to the very acid pH of the soil (3.0). Liming increased the P content of the plot 6 oat plants, but not to a normal level for oats.

Both plots 1 and 6 received an application of fertilizer, which contained 100 lbs./acre P, before the plots were sown. Therefore, the P levels of the soils should not have been deficient for the growth of oats. The low plant P levels, thus, seem to indicate that both soil acidity and liming lower the amount of plant available P in a soil.

The field results agree with Jackson (1969) who states that soil acidity decreases the plant availability of P.

(c) K Content of Whole Oat Plants:

Chapman (1966) stated that oat leaves at flowering should contain between 0.78 to 1.56 percent K in order to fall in the intermediate range. Oat straw is in the low range if the K percentage is less than 0.83.

For the oats grown on soils A and B in the greenhouse, the K level never fell below 1.8 per cent and ranged as high as 5.4 per cent. The oat plants from both soils A and B had a higher K content when grown on the $\text{Ca}(\text{OH})_2$ treatments as compared to the corresponding CaCO_3 treatment. For example, on soil A, the 60 tons/acre $\text{Ca}(\text{OH})_2$ treatment had a plant K content of 5.4 per cent while the 81.2 tons/acre CaCO_3 treatment had 2.9 per cent K (Table 22).

The K content of the oat plants was probably a reflection of the fact that the soils were fertilized with K. During the first cropping of soil A, there was no plant growth on the 60 tons/acre $\text{Ca}(\text{OH})_2$ treatment. Therefore, the oats grown during the second cropping were the first plants to grow on this treatment, and thus had the benefit of a higher nutrient level as compared to the other liming treatments. The K level of the oats grown on this treatment was the highest of all the treatments for both soils.

The oats grown on Waterton plots 1 and 6 possessed the same high K content as did the greenhouse oat plants (Table 23). The K percentage of the oats grown on plot 6 was, however, much lower in the 4 tons/acre CaCO_3 treatment than in the 29 tons/acre treatment (1.7% versus 2.4%). This was probably due to the very acid nature of the 4 tons/acre treatment (pH 3.0).

Since the plots and greenhouse soils were all

fertilized with K, the plants contained adequate levels of K. Thus, no conclusions could be drawn as to the general effects of soil acidity and liming on plant available level of K in the soil. But soil acidity did prevent the uptake of K by oats grown on the low lime treatment of plot 6 in quantities as high as that of the oats grown on the high lime treatment.

(d) Ca and Mg Content of Whole Oat Plants:

Chapman (1966) gives benchmark figures for deficient and intermediate levels of Ca and Mg for various stages of development for a number of plant species.

The oats from the greenhouse experiment using the acidified soils A and B were harvested at 6 weeks and had not yet developed heads. Chapman (1966) indicates that the intermediate range for Ca in the tops of young plants is 1.10 per cent Ca, and for the tops of plants at flowering is 0.26 per cent Ca. Since the greenhouse plants were closer to flowering, the results shown in Table 22 indicate that all treatments for both soils contained an abnormally high level of Ca. The lower rates of lime resulted in a decreased plant Ca level compared to the higher liming rates.

For Mg, Chapman indicates that the intermediate range for oats is 0.18 to 0.52 per cent Mg. For soil A (Table 22), the oat Mg level was above this range except

for the 60 tons/acre $\text{Ca}(\text{OH})_2$ treatment. This data reflected the extractable soil Mg content, where the 60 tons/acre $\text{Ca}(\text{OH})_2$ treatment contained a much lower extractable Mg than any of the other lime treatments (Table 20). The plant Mg status of oats grown on soil B fell within the intermediate range suggested by Chapman. This was, also, indicative of extractable soil Mg content which was much lower than for soil A (4.3 me/100 g. for soil A versus 0.40 me/100 g. for soil B).

The high Ca levels contained in the oat plants were expected due to the very high Ca in the soil as a result of liming. But, the large applications of Ca seriously altered the Ca:Mg ratio of the soils. Therefore, the question of whether or not excess Ca interfered with Mg uptake by plant tissue came to mind. By observing the data presented in Table 22 it would seem that Ca did not inhibit Mg uptake. For example, soil B had a low extractable Mg content, but the oats grown on this soil had a Mg status in the intermediate range.

Another observation made from the Ca and Mg results was the Ca:Mg ratios of the plant material. The soil ratio, after liming, was as wide as 30 to 1 and never less than 10 to 1. But in the oats grown on soils A and B the ratio was never wider than 4.5 to 1 and was as low as 1 to 1. Chapman (1966) indicates that a ratio of 2 or 3 to 1 is normal.

The whole oat plants analysed from Waterton plots 1 and 6 supported the previously discussed greenhouse results (Table 23). The Ca and Mg percentages were well above the intermediate range. As before, even though the soil Ca:Mg ratio was as wide as 18 to 1, the plant ratio was never greater than 2.5 to 1. Therefore, the uptake of Ca and Mg was regulated by the oat plants, and thus prevented a severe distortion of the natural Ca:Mg ratio of oat tissue.

(e) Na Content of Whole Oat Plants:

The Na content of oats grown on the greenhouse soils, A and B, exhibited a marked drop when the plants were grown on soils receiving $\text{Ca}(\text{OH})_2$ applications as compared to oats grown on the CaCO_3 treatments (Table 22). For example, the oats from the 30 tons/acre $\text{Ca}(\text{OH})_2$ treatment of soil A had a Na content of 0.08%, while the oats grown on the corresponding CaCO_3 treatment (40.6 tons/acre) had a Na level of 0.25%. The soil analysis results (Table 20) for extractable Na content of soils A and B did not reflect this trend.

Chapman (1966) indicates that less than 0.023% Na is an intermediate level for oat blades. Also, growth reduction was observed in oats containing between 1.15% and 2.50% Na. Thus, the results from Table 22 indicated a high, but not inhibitory, level of Na in the oats grown in

the first greenhouse experiment.

The oats grown on Waterton plots 1 and 6 reflected the soil Na levels. Plot 1 was located on a sandy, well-drained, knoll at Waterton (figure 1), which would indicate a low soil Na content. The oats from plot 1 had a low percentage of Na (0.005 to 0.006%). On the other hand, the Table 23 results indicated that the plot 6 soil (soil F) had a very high extractable Na content when compared to the other incubated soils. The plant Na content was, thus, much higher in the plot 6 oats (0.13% to 0.23%) than in the plot 1 oats.

The Na content of the oat plants did not exhibit any general trends. In the greenhouse experiment, a high rate of Ca(OH)_2 markedly lowered the Na uptake of oats grown on soil A. On the field plots, however, the Na levels of the oat plants were a reflection of the extractable Na in the soil.

(f) Mn and Al Content of Whole Oat Plants:

Chapman (1966) presents an intermediate range of 64 ppm to 140 ppm Mn and a deficient level of 10 ppm for 11 week old whole oat plants. The plant level where Mn is toxic is greater than 3,000 ppm.

The greenhouse oat plants had a range from 50 ppm to 590 ppm which indicates no deficient or toxic amounts of

Mn. From the greenhouse data, it was evident that plant Mn levels were proportional to the extractable Mn content of the soil, as stated by Bortner (1935). For instance, the low lime treatments of soil A (15 tons/acre Ca(OH)_2 and 20.3 tons/acre CaCO_3) showed a rise in extractable soil Mn due to the lowering of soil pH (Table 20). The oats grown on these treatments had a 3 to 4 times as high Mn level as compared to the higher liming rates.

Table 23 indicates that the Mn levels of the oats grown at Waterton were neither deficient nor nearing toxicity.

Chapman (1966) states that Al is not essential for plant growth. Therefore, he presents no values for Al content of oats. From the results of plot 6 (Tables 21, 23) it can be seen that Al uptake varied with soil Al levels, but to a lesser extent than did Mn. That is, the 4 tons/acre CaCO_3 treatment on plot 6 contained approximately 300 times the extractable Al as compared to the 29 tons/acre treatment; but the oat Al content from the low liming rate was only twice that of the oats grown on the high lime treatment. The pH of the 4 tons/acre treatment of plot 6 was 3.0 and the oat growth on this treatment was seriously inhibited by the soil acidity. But the Al content of these oat plants was not higher than the level in oats which exhibited no growth inhibition symptoms. Therefore, the oat plants did not have to absorb Al in order to be harmed

by Al.

(g) Fe and Zn Content of Whole Oat Plants:

The U.S. - Canada Feed Tables (1969) indicate that 500 ppm Fe is the intermediate level of Fe in oat hay. The toxic level of Zn in mature oat leaves is from 1,700 to 7,500 ppm Zn. A level of 20 ppm Zn is considered deficient in whole oat plants (Chapman 1966).

The oats grown on soils A and B had an Fe level well below the intermediate range for oat hay (Table 22). This indicated either a low soil Fe content or that liming prevented Fe uptake or translocation in quantities normally found in oats.

In contrast, the Zn content of the greenhouse oats was well above deficiency levels, but did not near toxicity levels for Zn (Table 22).

The oats grown on Waterton plot 1 had very low levels of both Fe and Zn. This was likely a consequence of total soil content of Fe and Zn rather than due to an adverse liming effect, as the fertility of the plot 1 soil was marginal because of the very sandy nature of the soil.

On plot 6, the oat Fe content was comparable to that of the greenhouse oat plants, but was less than the intermediate level (200 ppm versus 500 ppm Fe). The Zn

level of the oats was close to a deficient level. From these oat results for Fe and Zn content, there was no general trend that could be attributed to soil acidity or liming. Thus, variations in plant content of these elements was probably due to total Fe and Zn levels of the various soils.

2. Chemical Analysis of Oat Grain From the Innisfail Plots

The grain obtained from the Innisfail plots was analysed in order to compare the effect on plant composition of liming a neutral soil (Innisfail north plot) and of liming an acidified soil (Innisfail south plot). Also, the Innisfail south plot supported growth on all treatment sub-plots. Thus, the oat seed was analysed to compare plants grown on an unlimed and limed sulfur-acidified soil.

(a) N and S Content of Oat Grain:

The normal range of N in oat grain is 1.7% to 2.3% N (U.S. - Canada Feed Tables 1969).

The oat grain obtained from both the acidified (Innisfail south) and unaffected (Innisfail north) plots contained a total N level (2.2% N to 2.8%N) that was slightly above the normal range (Table 24). This was probably due to the application of N fertilizer to the plots.

The total S content of the grain did not reflect

Table 24. Elemental analysis of oat grain grown on acidified, limed, and normal soils at Innisfail.

Plot	Treatment	pH (Soil)	% N	% P	% K	% S
	Nil	5.4	2.2	0.28	0.50	0.16
North *	6 tons/acre Ca(OH) ₂	6.1	2.2	0.26	0.45	0.14
	Nil	3.5	2.7	0.17	0.30	0.12
South **	6 tons/acre Ca(OH) ₂	6.2	2.8	0.24	0.33	0.14

Plot	Treatment	pH (Soil)	% Ca	% Mg	ppm Na	ppm Al	ppm Mn	ppm Fe	ppm Zn
	Nil	5.4	0.09	0.14	76	7.8	72	44	63
North *	6 tons/acre Ca(OH) ₂	6.1	0.08	0.13	81	7.8	40	38	54
	Nil	3.5	0.07	0.10	61	15	80	53	42
South **	6 tons/acre Ca(OH) ₂	6.2	0.11	0.13	18	10	96	50	110

* North Plot - the plot is located on soil unaffected by sulfur.

** South Plot - the plot is located on sulfur-acidified soil.

the soluble sulfate content of the Innisfail soils. The results from Table 19 indicate that the sulfur-acidified soil (N) contained 1,400 ppm $\text{SO}_4\text{-S}$ while the normal soil (P) contained 41 ppm $\text{SO}_4\text{-S}$. However, the oat grain grown on the unlimed sulfur-acidified soil had a lower total S percentage than did the grain from the limed or unaffected soils. This suggests that the high sulfur assimilation observed in the greenhouse and field whole oat plants (Tables 22,23) was not accompanied by abnormally high S levels in grain obtained from these high sulfate soils.

Tisdale and Nelson (1966) stated that a normal N:S ratio for oat grain is, on the average, 16:1. The grain from the Innisfail north plot (normal soil) had N:S ratios of 14:1 (on the nil treatment) and 16:1 (on the limed treatment). On the Innisfail south plot, the N:S ratios were 22:1 (nil treatment) and 20:1 (lime treatment). These ratios indicated that the oat grain from the Innisfail plots was not abnormal as to the protein composition. The oat grain from the acidified plot (south) did have a slightly wider N:S ratio than did the grain from the normal soil. This was due to a higher uptake of N in the oats from the south plot, accompanied by a slight decrease in S assimilation in the grain from the nil treatment of the acidified soil (Table 24).

(b) P Content of Oat Grain:

The usual range for P in oat grain is 0.23%

to 0.55% P (U.S. - Canada Feed Tables 1969). The oat grain from the Innisfail plots was at the lower end of this range (Table 24). The oats from the unlimed acid soil had a P level of 0.17% which was below the normal range. The oat grain grown on the limed acid soil had a P content of 0.24%. The oats from the normal Innisfail soil (north) had P levels of 0.28% (nil treatment) and 0.26% (lime treatment).

As concluded for whole oat plants, the availability of P to the plant roots was lowered by soil acidity. Liming of the acid soil raised the availability of P, but not to the level of the normal, unlimed soil.

(c) K Content of Oat Grain:

The normal amount of K in oat grain ranges from 0.28% to 0.56% (U.S. - Canada Feed Tables 1966). The oats from both plots and treatments were within this range (Table 24), but the grain from the acidified plot was substantially lower than that from the unacidified plot (Innisfail north). Soil acidity caused a decrease, from 0.50% to 0.30%, in oat grain K content. Liming somewhat rectified this situation, but did not return the K level to that of the oats grown on the normal soil.

Both of the Innisfail plots received the same applications of K as a fertilizer. But, the K contents of the oats grown on these soils varied considerably. Thus, it was concluded that soil acidity and liming both decrease

K uptake by oat plants, as the unlimed normal soil produced oat grain with the highest K content.

(d) Ca and Mg Content of Oat Grain:

The U.S. - Canada Feed Tables (1966) indicate that the range for Ca content of oat grain is 0.03% to 0.19% Ca; and the Mg range is 0.15% to 0.23%.

The data from Table 24 showed that the Ca levels for the oats grown on the Innisfail plots, were in the normal range (0.07% to 0.11%). On the Innisfail south plot (the sulfur acidified soil) liming resulted in an increased Ca content of the oat grain (0.07% on the acid soil versus 0.11% on the limed soil). Lime had no effect on the Ca level of the oats grown on the Innisfail north plot (the unaffected soil).

The Mg levels, however, were all below the normal range of oat Mg content (Table 24); the oats from the Innisfail south (acidified soil) unlimed plot being the lowest. This was likely not a consequence of reduced availability of Mg due to soil acidity, but a maintenance of the natural Ca:Mg ratio by the oat plant. From the U.S. -Canada Feed Tables (1966), the Ca:Mg ratio of oat grain is 1.0:1.5. Hence, the lower Mg level in the oats grown on the unlimed acid soil was likely a result of the inability of the plant to absorb adequate amounts of Ca. These results pointed out, as did the analysis of the whole oat

plants, that the oat plants regulated their Ca and Mg uptake in order to maintain a natural Ca:Mg ratio.

(e) Na Content of Oat Grain:

The normal range for the Na content of oat grain is 280 ppm to 1,120 ppm Na (U.S. - Canada Feed Tables 1969).

The Na level of the oats grown on the Innisfail plots (Table 24) was well below this range. This was likely due to a low soil level of Na as neither liming nor soil acidity appreciably changed the oat grain Na content.

(f) Mn, Fe, Al and Zn Content of Oat Grain:

The intermediate Mn content of oat grain is 43 ppm, and the intermediate range of Fe in oat grain is 20 ppm to 140 ppm (U.S. - Canada Feed Tables 1969).

From Table 24, a comparison of the oat grain from acidified, limed and unaffected Innisfail soils indicated little effect of either acidity or liming on plant uptake and translocation of Mn or Fe. The oat content of Mn and Fe was within the normal range for oats; on both soils and treatments.

The Al content of the oat grain from the unlimed acidified soil (Innisfail south, nil) was only double that of the grain grown on the normal soils (Table 24). However, the extractable Al level of the acidified soil was very

much higher (Table 19). Therefore, Al, seriously inhibited the oat growth at Innisfail (acid soil) without being reflected by large quantities in the grain of the oat plants.

The Zn content of the oat grain indicated no trend corresponding to increases in either soil acidity or liming (Table 24).

Since the oat content of the micronutrients (Mn, Fe, or Zn) did not vary consistently with increases or decreases in soil acidity, the oat grain level of these nutrients was probably a consequence of the total soil levels.

3. Chemical Analysis of Whole Barley Plants

The barley samples were obtained from a greenhouse experiment. The object of the experiment was to obtain information as to the effect of extremely high lime applications (up to 50% of the soil weight) on plant growth. The soils used for the experiment were a very acid soil containing a large amount of elemental sulfur (soil K) and the unaffected soil from Waterton (soil I). The elemental composition of barley was determined to observe the effect of very large amounts of lime on the composition of plants grown on an acidified and normal soil.

(a) N and S Content of Whole Barley Plants:

The intermediate range for the N content of barley hay is 1.2% to 1.7% N (U.S. - Canada Feed Tables 1969). Barley straw is deficient in N if the level is less than 0.40% N, and the critical N level is 0.80% (Chapman 1966).

Five week old barley tops should contain about 0.27% S to possess an intermediate S level. Toxicity symptoms are prevalent if the S content exceeds 0.54% (Chapman 1966).

From table 25, it is evident that all barley plants contain an abnormally high level of N (3.2% to 6.4%), with the barley from the lower liming rates (42 tons/acre and 146 tons/acre) of the sulfur-acidified soil (K) having the largest N content.

The S values from Table 25 may indicate an additional cause of poor growth, besides high Al and Mn levels, on sulfur-acidified soils. Even after heavy lime treatments the soluble sulfate content of the 42 tons/acre and 146 tons/acre treatments of soil K was sufficiently greater to result in a barley S level of 1.2%. According to Chapman (1966), barley containing more than 0.54% S will exhibit sulfur toxicity symptoms.

The S content of the barley grown on the normal soil (I) was below the intermediate level of 0.27% for all

Table 25. Elemental analysis of whole barley plants grown on an acidified (soil K) and a normal soil (I) that had received extremely high amounts of CaCO_3 .

Soil	Treatment	pH (soil)	% N	% P	% K	% S
K	42 tons/acre CaCO_3	3.5	6.4	0.20	4.9	1.2
	146 tons/acre CaCO_3	6.5	4.2	0.25	3.8	1.2
	582 tons/acre CaCO_3	7.0	3.6	0.30	3.4	0.60
	Nil					
I	146 tons/acre CaCO_3	5.9	3.9	0.25	4.6	0.19
	582 tons/acre CaCO_3	7.0	3.6	0.24	4.4	0.19
		7.0	3.2	0.24	3.9	0.18

Soil	Treatment	pH (soil)	% Ca	% Mg	% Na	ppm Al	ppm Mn	ppm Fe	ppm Zn
K	42 tons/acre CaCO_3	3.5	0.88	0.54	0.05	38	125	210	140
	146 tons/acre CaCO_3	6.5	1.2	0.41	0.04	38	112	340	88
	582 tons/acre CaCO_3	7.0	1.1	0.39	0.06	56	100	370	100
	Nil								
I	146 tons/acre CaCO_3	5.9	0.88	0.28	0.02	50	62	225	120
	582 tons/acre CaCO_3	7.0	1.1	0.30	0.03	44	38	360	160
		7.0	1.1	0.29	0.06	38	25	310	140

treatments. A comparison of the barley grown on soils K and I indicated, conclusively, that the high levels of S exhibited by plants grown on sulfur-acidified soils was a result of the abnormally high sulfate content of these soils.

The above normal amount of N in the barley plants was probably due to the high level of soil N that resulted from fertilizing.

The N:S ratio of barley plants is 6.5:1 when grown on soils containing high levels of S (Tisdale and Nelson 1966). The N:S ratios of the barley grown on soil K ranged from 5.3:1 (on the 42 tons/acre treatment) to 6.0:1 (on the 582 tons/acre treatment). On the other hand, the barley from soil I (normal) had N:S ratios from 18:1 to 20:1. These results indicated that the large variations in N:S ratios, between the barley plants grown on soils K and I, were likely due to the wide differences in sulfate content between a normal soil (I) and a sulfur-acidified soil (K).

(b) P Content of Whole Barley Plants:

Chapman (1966) indicates that barley leaves at tillering stage should have an intermediate range of 0.27% P and a level of 0.17% P is considered low.

The barley plants obtained from the greenhouse experiment were harvested when green and not yet in the flag

leaf stage. The results from Table 25 indicate that the barley contained adequate levels of P on both soils for all treatments. For the barley grown on soil K (acidified soil), the low lime treatment (42 tons/acre CaCO_3) contained significantly less P than the high lime treatment (582 tons/acre CaCO_3) - 0.20% P versus 0.30% P, respectively. Since the 42 tons/acre CaCO_3 treatment had been reacidified, the uptake or translocation of P was decreased by the acidity. The barley grown on the normal soil from Waterton (soil I) had the same P content regardless of the treatment. That is, the barley from the nil treatment and the 582 tons/acre CaCO_3 treatment had the equivalent P status. Therefore, liming did not reduce the availability of P to the plant.

(c) K Content of Whole Barley Plants:

The critical level for barley K content is 0.92% in leaves and 1.01% in stems (Chapman 1966).

The barley from all treatments had a K percentage well above these critical levels (Table 25), due to a K fertilizer application. For barley obtained from both soils K and I, there was a slight decrease in the K content as the liming rates increased. This may suggest a minor interference by the very large concentration of Ca with the uptake of K.

(d) Ca and Mg Content of Whole Barley Plants:

The U.S. - Canada Feed Tables (1969) suggest that the intermediate level of barley straw is 0.34% Ca and 0.19% Mg. Chapman (1966) indicates that an intermediate level of Ca for young wheat plants is 1.38%, and 0.27% to 0.46% for Mg content of wheat plants.

From the data presented in Table 25 the barley grown on soils K and I contained intermediate to high levels of both Ca and Mg. As expected, the Ca percentage increased from 0.88% to 1.1% as the soil Ca level was raised by liming. The barley from soil K (acidified soil) decreased in Mg content as soil Ca increased (0.54% on the 42 tons/acre treatment). But the Ca:Mg ratio remained near the normal ratio of 2:1 for barley.

On soil I (normal), the Ca:Mg ratio decreased slightly with an increase in liming rate, but the total Mg uptake was not affected by liming. Thus, as previously discussed, a drastic alteration of the ratio of Ca to other soil cations, specifically Mg, in the soil was not reflected in the Ca and Mg content of plants grown on these highly limed soils.

(e) Na Content of Whole Barley Plants:

The intermediate range for Na content of barley leaves is 0.09% to 0.16% (Chapman 1966).

The results for barley analysis (Table 25) indicated

that barley for both soils and all treatments contained low levels of Na, but liming caused an increase in Na content of the barley grown on the normal Waterton soil (I). In soil K, the Na level of the barley was unaffected by liming.

The 3 fold increase in barley Na content observed when the normal soil (I) was limed, may have been due to the high Ca levels in the limed treatment. The saturation of the soil with Ca would have displaced any Na on the exchange complex into solution, thus, making the Na available to the barley roots.

(f) Al, Mn, Fe and Zn Content of Whole Barley Plants:

Chapman (1966) indicates that a level of 109 ppm Al in barley leaves is considered high and barley tops containing 770 to 1,000 ppm Mn have a toxic level of this element.

The U.S. - Canada Feed Tables (1969) indicate that 300 ppm Fe is the intermediate level for barley straw. Barley hay has an intermediate level of 39 ppm Mn.

Mature oat leaves will show toxicity symptoms when Zn levels are from 1,700 ppm to 7,500 ppm. Oats will have symptoms indicating Zn deficiency when the whole plant contains less than 20 ppm Zn (Chapman 1966).

As in the Mn content of whole oat plants, the

barley Mn level decreased as the liming rate increased. According to the literature (Morris 1948), the Mn content of plant tissue is well correlated with extractable levels of Mn in the soil. Therefore, the lowering of the amount of plant Mn was probably due to liming which lowered the soil Mn level.

The Al content (Table 25) of the barley was well below that indicated as high (109 ppm) by Chapman (1966). Since plant growth was harmed by soil acidity on the 42 tons/acre treatment, it was concluded, again, that Al uptake by the barley was not necessary in order for the Al to inhibit plant growth. Root injury by Al was probably the reason for the lack of healthy growth of barley on the acid soil.

The content of Fe and Zn (Table 25) was neither deficient nor approaching a toxic level for barley grown on all treatments of both soils. The Fe content of the plants showed an increase on the high lime treatments (146 tons/acre and 582 tons/acre) of both soils over the nil treatment (soil I) and the 42 tons/acre treatment (soil K). Thus, liming may have increased the availability of Fe in these soils, but the Zn level of the barley was not affected appreciably by soil acidity or liming.

Summary

The plant material grown on acid (pH 3.5), reclaimed, and nonaffected soils was analyzed to find whether or not acidity or liming significantly changed plant composition. The soil analyses (section D) showed that changes in pH altered the solubility of certain soil chemical constituents and liming greatly increased the Ca level of the soil. Thus, the limed and unlimed sulfur-acidified soils differed considerably in their chemistry, and both were different than normal soils located in the same vicinity. Even though all soils received N, P, and K fertilization soil acidity and/or liming may have resulted in alterations in normal plant composition. The following information was provided by plant analysis:

- (i) The N level was, for the most part, above normal in the plant tissue. This was probably a result of fertilization. The S content was very much above the usual level in the plants grown on the sulfur-acidified soils due to the very high sulfate content of these soils. The N:S ratios of the plant material were narrowed down to 5:1 on the limed and unlimed acidified soils and were in an average range in the plants from the normal soils (about 16:1).
- (ii) The plants grown on heavily limed soils had a P status equivalent to plants from normal soils. The plants from acid soils, however, had a lower P content than

the plants obtained from normal or lime neutralized soils.

- (iii) The plant levels of K, Ca, and Mg, were all lower in plants grown on acid soils as compared to those from the corresponding unacidified soil. Liming of the acid soils increased plant uptake of K, Ca, and Mg. As liming rate increased the plant Ca level increased. But there was no definite effect on plant K and Mg levels induced by overliming with CaCO_3 or Ca(OH)_2 .
- (iv) The amount of Na in oat or barley tissue did not show a definite trend which could be attributed to either soil acidity or liming. CaCO_3 , however, promoted a greater Na uptake than did Ca(OH)_2 .
- (v) In the case of the micronutrients Mn, Al, Fe, and Zn, acidity and liming only produced consistent variations in the uptake of Mn. The plant level of Mn varied with soil pH. That is, liming reduced plant uptake of Mn. On the other hand, plant Fe, Zn, and Al levels were not lowered by liming. Any deficient levels of Fe or Zn would likely be a result of low total levels in the soil, rather than due to soil acidity or liming.

V. SUMMARY AND CONCLUSIONS

Investigations conducted at the Shell Canada gas processing plant near Innisfail Alberta had shown that liming restored plant growth to one mildly sulfur-acidified soil (Nyborg and Schurer 1972). At the Waterton plant an acidity problem had developed that was much more widespread than at Innisfail. The soils that comprised the acidified area at Waterton had a wide range of pH values (1.5 to 4.0) and varying levels of unreacted elemental sulfur. Therefore, in reclaiming the soils it was considered necessary to neutralize present acidity as well as that resulting from oxidation of unreacted elemental sulfur. Because of this, and due to the variations in soil pH, some soils would inevitably be overlimed in the process of reclamation.

Field, greenhouse, incubation, and laboratory experiments were undertaken, using a variety of soils, with the objectives of determining the form, amount, and placement of lime necessary to return plant growth to sulfur-acidified soils; and determining the effect of acidity and liming on soil and plant chemical composition. A secondary incubation experiment had the purpose of determining rate and amount of sulfur oxidation in soils, and to find how acid soils would become from sulfur oxidation.

From these experiments the following observations

and conclusions were drawn.

1. The form of lime best suited for use in reclaiming sulfur-acidified soils was CaCO_3 . The soil-neutralizing ability of CaCO_3 was similar to that of Ca(OH)_2 , and excess amounts of CaCO_3 did not raise the soil pH above 7.5 and promoted good, normal plant growth. On the other hand, Ca(OH)_2 applied at rates above that required for soil neutralization raised the pH to a point inhibiting plant growth.
2. When comparing CaCO_3 and MgCO_3 as to their ability to reclaim sulfur-acidified soils, it was found that MgCO_3 did not lower the soluble- SO_4 level sufficiently to prevent plant injury due to soil salinity. Crushed limestone containing more than 5% MgCO_3 was of little value in reclaiming a sulfur-acidified soil.
3. The amount of lime required to reclaim a soil made acid by sulfur oxidation was that amount which neutralized present acidity plus the acid produced from elemental sulfur oxidation induced by liming.
4. When applying lime to a soil, it should be incorporated as deeply as possible into the soil. The downward diffusion of lime was insufficient to neutralize acid soil below the depth of lime application. Since plant roots are not viable in acid soil, the root zone of deep acid soils will be very shallow. Thus, in times of low precipitation, plants grown on these soils will be

subject to moisture stress.

5. After additions of sulfur to normal and limed soils, the sulfur was quickly oxidized and lowered the pH to 2.5. The oxidation rate was most rapid in a limed soil that was previously acidified.
6. The chemical analysis of acidified, limed, and unaffected soils indicated that high soil solution levels of Al (and in some instances Mn and SO_4) was the primary cause of soil sterility in the sulfur-acidified soils.
7. Liming of acidified soils with CaCO_3 or Ca(OH)_2 decreased the extractable Al and Mn to non-toxic levels, somewhat lowered the solubility of SO_4 , and drastically altered the Ca:Mg ratio of the soils.
8. The mineralization of N (both chemical and biological) in sulfur-acidified soils resulted in accumulation of ammonium to approximately the same extent as that found in normal soils. There was virtually no nitrification in soils of pH 4.5 or lower. Liming eventually restored the ability of the soils to nitrify.
9. The analysis of oats and barley grown on acidified (pH 3.5), limed, and unaffected soils indicated that soil acidity did not result in an abnormally low N:S ratio, decreased the availability of P to the plants, and increased the plant uptake of Mn. Also, liming did not result in an abnormally high Ca:Mg ratio within the plant, increased the P uptake of plants (but not to the level of P present in plants grown on normal soils), and

increased plant uptake of Ca, Mg, and K.

The greenhouse and field plot experiments, and the chemical analysis of soils and plants indicate considerable resistance of soils to permanent damage and infertility. At Waterton, much of the soil had been acidified to pH 2.0 for a period of up to ten years. The large concentrations of sulfuric acid in the soils had seriously altered many of the microbial and chemical processes normally found in unaffected soils. But after liming, the soils readily regained their fertility and were able to produce good, normal plant growth.

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Appendix I. pH and elemental sulfur content of soil A (incubation).

Treatment	0 days	3 days	9 days	27 days	81 days	243 days						
	pH	S° (ppm)	pH	S° (ppm)	pH	S° (ppm)						
Nil	2.0	588	2.0	645	1.8	602	2.2	629	2.4	626	2.6	499
15 tons/acre Ca(OH) ₂	6.8	558	6.3	624	6.2	583	6.1	569	5.4	257	5.0	172
30 tons/acre Ca(OH) ₂	9.5	555	9.2	610	9.2	599	8.2	577	8.2	485	8.0	404
60 tons/acre Ca(OH) ₂	12.2	473	11.4	482	12.3	521	11.2	587	9.8	430	8.2	375
20.3 tons/acre CaCO ₃	6.8	640	6.6	575	6.7	570	6.0	579	5.9	370	5.2	159
40.6 tons/acre CaCO ₃	7.0	600	7.2	587	7.4	585	7.3	554	7.4	454	7.4	192
81.2 tons/acre CaCO ₃	7.2	623	7.3	635	7.5	615	7.4	517	7.5	293	7.4	189

Appendix II. pH of soil B (incubation).

Treatment	Soil pH					
	0 Days	3 Days	9 Days	27 Days	81 Days	243 Days
Nil	3.4	3.3	3.0	3.1	3.2	3.4
5 tons/acre Ca(OH) ₂	6.3	5.8	5.4	5.0	4.8	4.8
10 tons/acre Ca(OH) ₂	8.2	7.9	7.9	7.4	6.9	6.7
20 tons/acre Ca(OH) ₂	9.6	9.5	9.6	8.2	8.0	7.8
6.5 tons/acre CaCO ₃	6.3	5.9	5.6	5.0	4.8	4.6
13 tons/acre CaCO ₃	7.2	7.2	7.2	6.8	7.0	6.8
26 tons/acre CaCO ₃	7.3	7.2	7.4	7.2	7.4	7.3

Appendix III. Dry weight yields of grasses grown on soil A.

Treatment	Fescue			Timothy		
	1st Cutting	2nd Cutting	3rd Cutting	1st Cutting	2nd Cutting	3rd Cutting
Nil	0.00b	0.00b	0.00c	0.00b	0.00c	0.00c
15 tons/acre Ca(OH) ₂	0.69a	2.59a	3.25a	0.97a	2.67a	2.22ab
30 tons/acre Ca(OH) ₂	0.06b	0.14b	0.33c	0.03b	0.20c	0.05c
60 tons/acre Ca(OH) ₂	0.00b	0.00b	0.00c	0.00b	0.00c	0.00c
20.3 tons/acre CaCO ₃	0.80a	2.18a	2.76b	1.07a	2.75a	2.41a
40.6 tons/acre CaCO ₃	0.87a	2.36a	3.56a	1.02a	2.03b	2.09b
81.2 tons/acre CaCO ₃	0.80a	2.02a	3.46a	0.94a	2.16ab	1.87b

* Treatment results not followed by same letter are significantly different at the 1% level.

Appendix IV. Dry weight yields of grasses grown on soil A.

Treatment	Yields of dry matter (g/pot)			
	Crested Wheat		Brome	
	1st Cutting	2nd Cutting	3rd Cutting	1st Cutting 2nd Cutting 3rd Cutting
Nil	0.00c*	0.00b	0.00d	0.00c 0.00b 0.00b
15 tons/acre Ca(OH) ₂	0.18abc	0.84ab	0.95b	0.29bc 2.10a 2.52a
30 tons/acre Ca(OH) ₂	0.03bc	0.04b	0.10d	0.12cd 0.27b 0.76b
60 tons/acre Ca(OH) ₂	0.00c	0.00b	0.00d	0.00d 0.00b 0.00b
20.3 tons/acre CaCO ₃	0.34ab	1.12a	0.97ab	0.54a 2.01a 2.72a
40.6 tons/acre CaCO ₃	0.49a	1.07a	1.27a	0.49ab 1.79a 2.10a
81.2 tons/acre CaCO ₃	0.36a	1.01a	0.57c	0.64a 1.69a 3.21a

* Treatment results not followed by same letter are significantly different at the 1% level.

Appendix V. pH and elemental sulfur of soils A, L, M, and Q after sulfur added.

Soil	Treatment	0 weeks			3 weeks			6 weeks			12 weeks		
		pH	S° (ppm)	pH	S° (ppm)	pH	S° (ppm)	pH	S° (ppm)	pH	S° (ppm)	pH	S° (ppm)
A	Nil	1.5	620	2.1	610	2.2	880	2.3	500				
	S*	1.6	1.1 x 10 ⁴	2.0	7.5 x 10 ³	2.2	6.6 x 10 ³	2.2	7.0 x 10 ³				
L	Nil	3.0	0.0	3.4	0.0	3.4	0.0	3.5	0.0				
	S	2.9	1.0 x 10 ⁴	2.6	7.2 x 10 ³	2.4	4.2 x 10 ³	2.4	3.2 x 10 ³				
M	Nil	5.5	trace	5.2	trace	5.2	0.0	5.2	0.0				
	S	6.0	1.0 x 10 ⁴	2.5	3.9 x 10 ³	2.4	1.9 x 10 ³	2.5	1.1 x 10 ³				
Q	Nil	5.9	0.0	5.8	0.0	5.7	0.0	5.8	0.0				
	S	5.8	1.0 x 10 ⁴	4.4	6.4 x 10 ³	3.0	3.8 x 10 ³	2.6	1.6 x 10 ³				

* S denotes that sulfur was added to the soil at a rate of 1% of the soil weight.

APPENDIX VI

pH of soils C and D from laboratory tube experiment
concerning downward movement of lime in bush soils

Treatment	Soil	Depth	pH
Nil	Intact *	0-1	2.4
		1-2	2.8
		2-3	2.8
		3-7	2.8
	Surface removed**	0-1	3.0
		1-2	3.0
		2-3	3.0
		3-7	2.9
20 tons/acre CaCO_3	Intact	0-1	7.2
		1-2	5.4
		2-3	3.0
		3-7	2.8
	Surface removed	0-1	7.8
		1-2	4.8
		2-3	3.1
		3-7	2.8
20 tons/acre Ca(OH)_2	Intact	0-1	11.6
		1-2	5.1
		2-3	3.0
		3-7	2.8
	Surface removed	0-1	11.8
		1-2	4.1
		2-3	3.0
		3-7	2.8

* Intact designates soil as found in bush.

** Surface removed designates that the sulfur containing
surface inch of soil removed.

APPENDIX VII

Modified Hart (1961) Method for Determining Elemental Sulfur Levels in Soil and Water

1. Preparation of a Standard Curve:

Dissolve 0.01 g. elemental sulfur in 100 ml. of reagent grade acetone to prepare a stock solution. Pipette 2, 4, 6, 8, 10, 15, and 20 ml. of stock solution into 100 ml. volumetric flasks. Add enough acetone to each flask in order to have a 20 ml. volume of acetone in the flasks. Add distilled water to each flask, while agitating, to bring the total volume to the mark. Allow the solutions to sit for one hour to permit optimum color development. The solution turbidity is then determined on a colorimeter set at 430 mu. Plot the results on semi-log graph paper with ppm elemental sulfur versus per cent transmittance.

2. Determination of Elemental Sulfur in Soils:

Oven-dry the soil at 70°C overnight to eliminate any possible error due to variations in soil water content. Pass the soil through a 16 mesh seive before extracting. Extract the soil in acetone for one half hour using plastic, round-bottomed, centrifuge tubes. Be sure the tubes are stoppered with cork stoppers as rubber contains sulfur. Use a shaker, for extraction, which gives a reasonably vigorous agitation to the solution.

After shaking, centrifuge the solution at approximately 2,000 r.p.m. for 15 minutes to remove any suspended

particles from the solution.

Take a suitable aliquot of the supernatant (2.0 ml. to 20 ml.) and pipette into a 100 ml. volumetric flask. Make the volume to the mark with distilled water and allow to sit for one hour. Then determine the per cent transmittance. Determine the concentration of sulfur in the soil by use of the standard curve.

When dealing with sulfur-acidified soils, the level of elemental sulfur in the soils varies widely. Thus, extraction ratios and aliquots must be adjusted accordingly.

When extracting a soil, it is desirable to have a low acetone to soil ratio in order to increase the accuracy of the determination. But, the solubility of sulfur in acetone is only 400 ppm. Thus, many soils will exceed the solubility range except when a very small sample is extracted in a large volume of acetone.

For most soils, a ratio of 1 g. of soil in 30 ml. of acetone is suitable. But, a soil containing more than 10,000 ppm elemental sulfur (10 tons/acre) will exceed the solubility of sulfur in acetone when this 30 to 1 extraction ratio is used.

In order to determine the correct extraction ratio to employ, use the following trial and error method. Extract the soil with the 30 to 1 ratio. If a 2 ml. to 20 ml. aliquot of extraction solution yields a reading of more than 15 per cent transmittance, then the solubility range has not

been exceeded. If a 2 ml. aliquot (do not use an aliquot less than 2 ml.) reads less than 15 per cent, then the solubility limit is being approached. Therefore, re-extract the soil using more acetone or less soil (do not use less than a 0.5 g. sample).

3. Determination of Elemental Sulfur in Run-off Water:

Pass the water sample through a #42 filter paper to remove all suspended particles from the soil. Dry the filtrate (plus filter paper) in an oven at 70°C. Measure the volume of water from which the filtrate was obtained.

After drying the filtrate, place it in a 500 ml. erlenmeyer flask and add acetone at one of the following rates: if there is no visible sulfur add 200 ml. of acetone; if a few particles are visible add 300 ml.; and if a number of particles of sulfur are visible add 400 or more ml.

Shake the solution for one half hour to dissolve the sulfur. If some sulfur is still visible in the bottom of the flask, shake the solution for 2 hours. After 2 hours, if any sulfur remains, add more acetone and continue shaking the solution.

When all sulfur is dissolved, take a 2 ml. to 20 ml. aliquot of solution and determine the level of elemental sulfur in the water as described for soil.

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